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THE ANALYSIS OF NON-FERROUS ALLOYS

F. IBBOTSON
AND
L. AITCHISON



**THE ANALYSIS OF
NON-FERROUS ALLOYS**

THE ANALYSIS OF STEEL-WORKS MATERIALS

By HARRY BREARLEY

AND

FRED IBBOTSON, B.Sc. (LOND.)

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INTRODUCTION TO METALLOGRAPHY

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Technical High School, Aachen.

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THE ANALYSIS OF NON-FERROUS ALLOYS

BY

FRED IBBOTSON

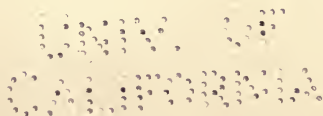
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PREFACE

It is probable that a true estimate of the importance and degree of self-realisation of a subject (or branch of a subject) may be found in the literature to which it gives rise. Judging the analytical chemistry of the non-ferrous alloys from this point of view, it may be seen at once that its importance is of very recent growth, and that even now it is very far behind its sister-rival, the chemistry of the ferrous alloys. Fortunately there are abundant signs that the makers and users of non-ferrous alloys are determined to utilise scientific knowledge and progress to a much greater extent than formerly, and the first essential in any of these advances is accurate chemical analysis. This has resulted in the appearance of a large mass of scattered information in the technical and chemical journals. Generally these have had in view two aims—first, accuracy combined with convenience; and secondly, accuracy combined with speed. Anyone who has worked through the analysis of an alloy by the methods outlined in the standard text-books of practical chemistry will realise at once that the time-honoured processes, redolent of unlimited time and sulphuretted hydrogen, fulfil neither of these two conditions. The aim of this book is to bring within the covers of one volume the methods which in the authors' opinion and experience combine as far as possible both these qualifications in the highest degree. A further aim has been to make possible the estimation of one element without the tedious separation from every other element which so often occurs in the older text-books.

In view of the huge number of original papers that have appeared and are still appearing on this subject, this book cannot be more than a milestone on the road to greater accuracy and higher speed. At the same time it will be

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found that the methods recommended are quite fitted to the needs of the works' chemist and at the same time are eminently suitable for use in the laboratories of all institutions whose curriculum embraces the analysis of alloys. In order to meet these two classes of students more thoroughly, the work is so arranged that the metals that are to be met with in the course of the analysis are treated from the point of view of pure solutions or pure substances, and this is followed by a chapter in which all the various alloys are treated separately, when the more suitable methods applicable to these alloys are detailed.

The courtesy of the Council of the Chemical Society in allowing Figs. 14, 15, 16, 17 and 19 to be reproduced from their *Transactions* must be acknowledged gratefully. Fig. 13 is reproduced from the *Chemical News* by kind permission of the editor.

F. I.

L. A.

METALLURGICAL DEPARTMENT,
SHEFFIELD UNIVERSITY,
July 1914.

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The Analysis of Non-Ferrous Alloys

CHAPTER I

APPARATUS FOR ELECTROLYTIC ANALYSIS

DURING the last few years the employment of electrolytic methods in the analysis of commercial alloys has increased by leaps and bounds. The various improvements that have been effected in the different parts of the apparatus that are required have kept pace with the demand, with the result that anyone wishing to set up an apparatus for the work has an almost infinite choice of arrangements. Naturally there has been but little alteration in the source of current supply, though in more recent times the employment of very much heavier currents and greater E.M.F.'s has produced some fairly large and complicated arrangements for the work. As a rule, for purely analytical work, the currents vary between 0.05 and 10 to 15 amperes, whilst the fall of potential across the electrodes of the cell in which the deposition is to be effected varies from 1.0 to perhaps 20 volts. The higher values are employed only for the very rapid analytical methods using a mechanical agitation of the solution. It is fairly obvious that if this range is to be obtained from ordinary lead accumulators some rather complicated arrangement of the apparatus is to be expected. Many of the older workers (and probably more recent ones who have no other or better facilities) obtained their current from the electric light circuit. This involved the use of a transformer which was not too economical, as it meant that the transformation must give the maximum voltage that

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was likely to be required. When anything less than this was being used (and in general this was the case), much energy had to be dissipated by the use of lamps and similar resistances in the circuit. Then, too, the amperage that is desired is not always obtainable easily. As a result the use of this source of energy was neither economical nor neat.

For ordinary purposes the best arrangement is a low voltage dynamo and a large battery of lead accumulators. As a rule these two work together, the dynamo being used to charge the cells, which then act as distributors. A typical arrangement has a dynamo directly coupled with a 3 H.P. motor generator. The motor is fed from the ordinary town supply (200 volts) and uses 8 amperes. This gives 1400 revolutions, which in the dynamo produces 8 volts at 150 amperes. In general 25 per cent. of overloading is allowable—thus bringing up the voltage to 10. If required, the current from the dynamo may be used directly by a suitable arrangement of resistances, but it is better to send it into the storage batteries. These are the usual large lead accumulators of capacity each 10 ampere-hours and voltage 2. By having a sufficiency of these almost any desired current and E.M.F. within the limits stated above may be obtained. Twelve cells are generally enough to give the necessary E.M.F. For the 2-volts circuit two or more are taken in parallel, and for the higher voltage the necessary number in series may be employed. It is well to have the accumulators arranged in two sections so that one half may be charged whilst the other half is supplying current. It is advantageous to have the terminals of each cell or pair of cells connected to a switchboard so that the worker can employ his own arrangement of cells in series or in parallel according to whether he desires a high voltage or a low resistance. Such an arrangement is better than a set of fixed plugs and a few voltages.

The circuit employed is bound to necessitate the use of various resistances. For an ordinary apparatus the resistance required can be obtained by having a rheostat in each separate deposition circuit. The most convenient form,

APPARATUS FOR ELECTROLYTIC ANALYSIS 3

undoubtedly, is the sliding contact resistance (Fig. 1). These can be obtained in various sizes, and the one most suitable to the circuit may be employed. If measurements of the resistances are required this form is not so suitable, neither

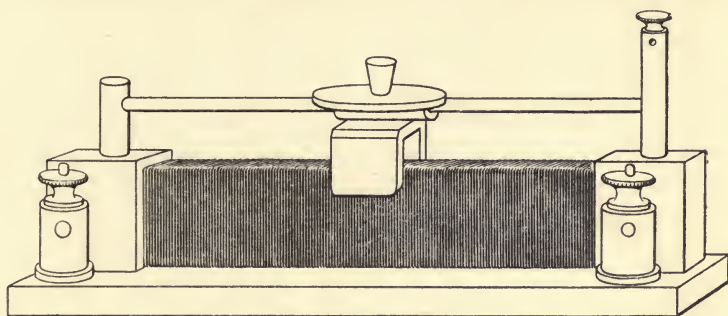


Fig. 1.

as a rule is it fitted for the production of a high resistance. For measurements a good arrangement is the switchboard and coils shown in Fig. 2. This may be conveniently arranged to work between 0.1 and 20 ohms or more. Such high resistances as may be required occasionally, are obtained

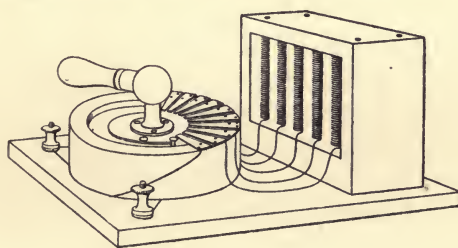
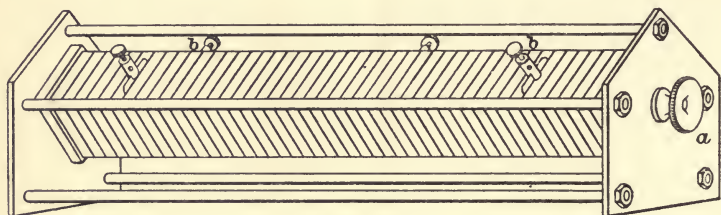


Fig. 2.

best by larger installations. Liquid resistances may be employed for some of these arrangements, but they are not very good to work with, if very constant currents are required. The principal drawbacks in these are due to the evaporation of the liquid. As a rule a solution of some cheap alkaline salt is employed, and the heat generated in the solution is sufficient to cause a fairly rapid loss of solvent.

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This exposes part of the electrodes, and as a result changes the resistance. Also, the exposure means that the electrodes suffer eventually from corrosive effects if they are at all liable to oxidation. Further, the introduction of a liquid resistance means the possibility of back E.M.F.'s in the circuit—another undesirable thing. Although they are useful for working with heavy loads, the electrolytic apparatus is too delicate for any extensive use of this type of resistance, except under special circumstances. Another resistance which is of great use if fairly heavy currents are being used, is the carbon block resistance (Fig. 3). The blocks may be obtained of various surface areas and consequently can be made to give different resistances. By tightening and



a. Regulating screw.

FIG. 3.

b, b. Copper strips.

loosening the grip *a* the resistance is altered. The brass or copper strips, *b, b*, that are introduced at intervals among the plates allow of various resistances being employed.

Having obtained the requisite current, it is necessary usually to measure both the current density and also the fall of potential across the electrodes. The latter is necessary, for the mere statement of the E.M.F. at the ends of the circuit is not at all valuable. The accurate estimation by electrolytic means requires that the potential fall of the cell should be known, and this is always much smaller than that at the ends of the circuit. The most usual method is to shunt the voltmeter across the terminals of the electrolytic stand (*c.f.* below), and this may be taken as very fairly representative of the difference of potential between the two electrodes, always providing that the contacts between the terminals of the stand and the electrodes are quite good.

As a rule the voltmeter circuit should contain a tapping key so that the current only goes through the instrument when the key is pressed down, which need not be very often. Also the voltmeter employed should be one of very high internal resistance. When the voltmeter circuit is closed the current has two paths open to it, one through the cell and the other through the voltmeter. Both of these obey Ohm's Law, and hence the resistance between the two terminals is lowered by an amount which is greater or less according as the resistance of the voltmeter is low or high. (If r_1 be the resistance of the cell, r_2 that of the voltmeter, and R that of the combination, then $\frac{1}{R} = \frac{1}{r_1} + \frac{1}{r_2}$ i.e. $R = \frac{r_1 r_2}{r_1 + r_2}$)

Evidently as r_2 increases, the value of R approximates more closely to that of r_1 , and hence there is less change of resistance on closing the voltmeter circuit.) A change of resistance between the terminals means a change of potential difference, and as a result the voltmeter, although measuring the potential difference existing at the time of the closed circuit, does not measure the potential difference existing with the voltmeter circuit open and which, of course, is the important information. By making the internal resistance high, the change of resistance is sufficiently slight to allow the values of the potential difference to be taken as representing the state of affairs with either closed or open circuit. (The question of E.M.F. is amplified later in connection with Sand's apparatus, p. 13.) In the sequel the E.M.F. which is mentioned will be taken to be this potential difference across the electrodes, measured in this way.

Current density is defined usually as the ratio of the amperage of the circuit to the area of the kathode expressed in square decimetres, and in all the sequel this is the significance of the term. The current is measured usually by some form of ammeter—or by a galvanometer if circumstances allow it. The ammeter should be of such range that the current can be read to 0.02 amperes, between zero and 15 amperes. Generally this would be too much of a tax for most instruments and the difficulty may be over-

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come in either of two ways. Two ammeters may be used, one reading up to 5.0 amperes and the other being extended only for the range above 5.0 amperes. The more contracted scale in the case of the second instrument is not so important, as the accuracy required in the measurement of fairly large currents is not so great as in the lower ones. The other method is to use a shunt in conjunction with the ammeter. This requires that the internal resistance of the ammeter shall be known accurately. Then, as in the case of the voltmeter, when the shunt is put in, the current has two paths

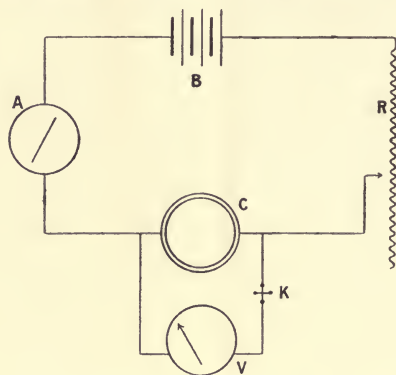


FIG. 4.

A. Ammeter.
C. Electrolytic cell.
V. Voltmeter.

B. Battery.
R. Rheostat.
K. Tapping key.

and divides itself between the two paths in the inverse ratio of the resistances of these paths. (Hence if the resistance of the ammeter be r_1 and that of the shunt r_2 the proportion of the original current c passing through the galvanometer is $\frac{r_2 c}{r_1 + r_2}$, which may be known quite accurately. In general, to find the required value of resistance for the shunt, it should be $\frac{r_1}{n-1}$ in order to reduce the current in the galvanometer to $\frac{1}{n}$ th of its original value.) In general there is no objection to putting the ammeter in the main circuit. The circuit required is shown in Fig. 4.

The actual electrolysis is performed between metal

electrodes which are connected in a suitable manner to the source of current. The forms of electrode are very numerous. Originally only platinum, or an alloy of platinum with another metal of its group (rhodium or iridium), was employed for both anode and kathode. The earliest depositions were made always upon a platinum dish. This was the kathode, and by means of a simple binding screw the wire conveying the current was attached. Dish electrodes vary in capacity, a fairly representative one holding about 180 c.c. of electrolyte, and weighing about 50 grams. The anode used in

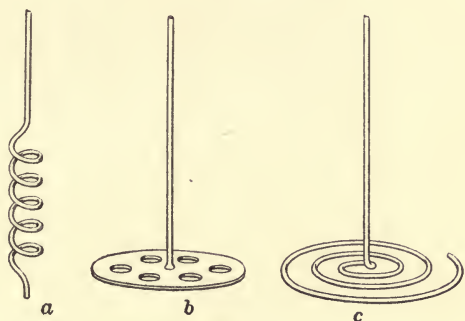


FIG. 5.

connection with this was often just a loop of moderately stout platinum wire. Later this was extended into a more substantial arrangement, particularly when it was realised that occasionally anodic deposits were valuable. This led to the use of the spiral, or the perforated disc, or the flat ring (Fig. 5, *a*, *b*, *c*). Of these the most convenient (though not the cheapest) is the perforated disc, from which the removal of an anode deposit is performed quite easily. The use of the dish electrode is quite satisfactory under certain circumstances, but not at all convenient under others. The capacity of the dish is such that for electrolytes of small solubility the preparation of a suitable solution is a matter of difficulty, as it contains too little of the metal which is to be deposited (electrolytes containing ammonium oxalate are good examples of this). An increase in the size of the dish

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is not possible on the scores of expense and convenience. The low capacity tells again in those cases when the solution to be electrolysed is obtained after a series of other analytical operations resulting in the production of a fairly large bulk of liquid. To evaporate this to about 50 or 70 c.c., as is required by the dish, means the expenditure of more time than most analysts care to spend. As a result of this the dish electrode was soon superseded by a separate kathode which was suspended along with a separate anode within a beaker or other convenient glass vessel containing the electrolyte.

The earliest forms of kathode to be employed in this way were just ordinary platinum crucibles soldered autogenously to a stout platinum wire. This was followed by the cone electrode (Fig. 6). Naturally these were rather heavy, and, although reasonably convenient to clean, did not offer the maximum of surface with the maximum of mass. Further, it was found that for many deposits a smooth surface (approximately plane) was not conducive to the production of the most satisfactory deposits. (This is connected with the phenomenon of over-voltage, *cf.* p. 32.) At first the difficulty was overcome by sand blasting the electrodes, but later the use of platinum gauze became almost universal. The various forms of gauze electrode with their corre-

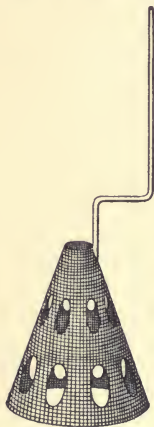


FIG. 6.

sponding anodes are shown in Fig. 7. The one of these that is most convenient is determined chiefly by the special conditions of the deposition. For stationary depositions the form (b) is most convenient, whilst for rotatory depositions (c) has the advantage that the rotating part is light, whilst it has the disadvantage that the rotating part is never the one on which the deposition is being made. Similarly, of course, the opposite objection, that the rotating part is always the one on which the metal is being deposited, applies to (b) when it is used in rotatory depositions.

The stands that are in use with different forms of elec-

trode naturally are a little varied. The stand shown in

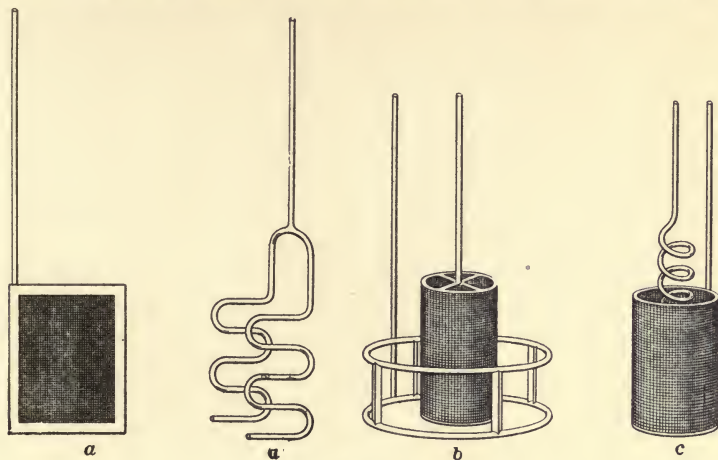


FIG. 7.

Fig. 8 is admirable for use with the dish kathode. It has a ring of brass into which are fixed three small platinum tips which protrude slightly and on which the dish is able to rest, thus ensuring good electrical contacts. The anode is suspended from a separate arm, the end of which is insulated from the upright. The kathode connection is *via* the upright to a terminal (*a*), whilst the anode is attached by a loose wire in the head of the upright, down the centre of which runs a connection to the terminal (*b*). This stand is quite useless for the separate electrodes—such as the various gauze forms. For these the separate stands are used as in Fig. 9. If it is desired to have the whole apparatus in a compact and convenient form the arrangement shown in Fig. 10 is very satisfactory. This has all the necessary

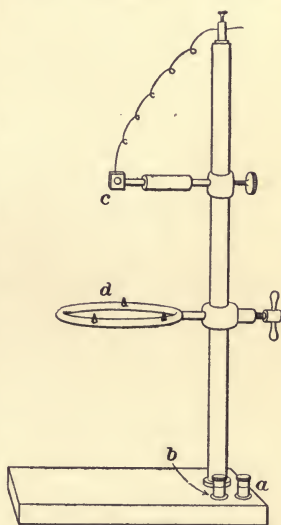


FIG. 8.

- a.* Kathode terminal.
- b.* Anode terminal.
- c.* Anode support.
- d.* Kathode support.

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parts very easily accessible. The figure shows the necessary

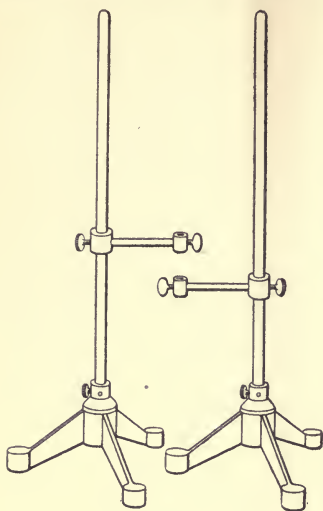


FIG. 9.

arms to be movable either vertically or in a horizontal plane. The electrolyte is contained in a very wide-topped tap funnel, thus allowing of the rapid and easy removal of the electrolyte from the electrode without any stoppage of the current if this is desired. The voltmeter, ammeter and rheostat, are all seen in position on the same stand, thus producing a very neat and compact form of apparatus suited to the use of those who are doing electrolytic analysis for the result only. The stand requires no setting up, but if it goes wrong

will take much longer to put in order than does an ordinary apparatus set up by the worker

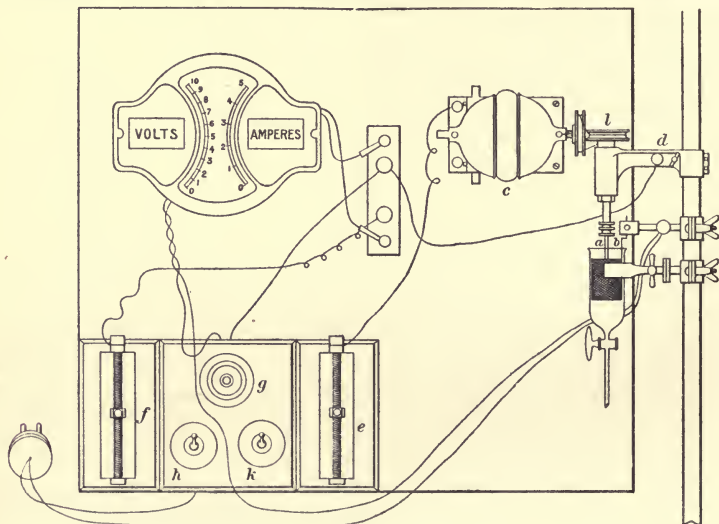


FIG. 10.

- a. Anode.
- b. Kathode.
- c. Motor to provide rotation.
- d. Movable arm.
- e, f. Rheostats (motor and electrolysis circuits).
- g. Tapping key for voltmeter.
- h, k. Switches for two circuits.
- l. Rotating head.

himself in which the important connections are not hidden. The apparatus has a small motor attached with which to rotate one electrode—generally the anode. The head of the grip for this electrode is provided with the necessary pulleys.

When rotation is desired with the apparatus of Fig. 9, a different head for the gauze electrode is employed (Fig. 11). The rotation may be produced by any suitable means. A small electric motor is very satisfactory and is easy to instal, whilst a water turbine may be used under most circumstances and has the advantage of running quietly. Usually the various arrangements for rotating the electrodes are matters of manufacturers' details rather than anything else. The only other interesting method for rotation is that in which the solution itself is made to rotate quite apart from any movement of the electrodes. This is effected by the use of

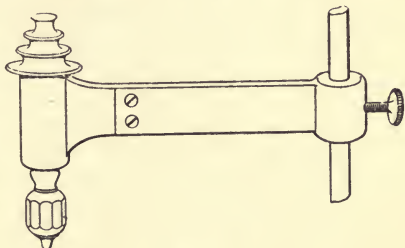


FIG. 11.

a magnetic field round the electrolytic cell. The beaker rests upon a thick iron hollow cylinder, and this rests upon an iron base. This base also supports a solenoid of fairly thick copper wire (1.5 mm.), the total resistance being about 1 ohm. The same current that is used for the deposition is passed through this coil, the result being that the electrolyte rotates at a very satisfactory speed. In some arrangements the stirring is done quite apart from the electrodes, a separate stand carrying a glass stirrer of various designs being employed.

Very frequently it is desirable to heat the electrolyte to some temperature well above the ordinary in order to accelerate the deposition. In the case of the dish this may be done quite well by having a rose burner below an asbestos pad which is several centimetres below the dish. By a careful regulation of the burner most desired temperatures may be obtained. In the case of the gauze electrodes the

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same kind of arrangement is possible if the beaker be used and supported upon a tripod or similar stand. It is just as satisfactory to surround the cell with a rather stronger vessel in which some other liquid may be heated. In the case of very rapid analyses, the solution if put in hot will probably maintain its temperature by the heat produced in the cell. Whenever the analysis takes more than twenty minutes or half an hour there is bound to be a loss of electrolyte by

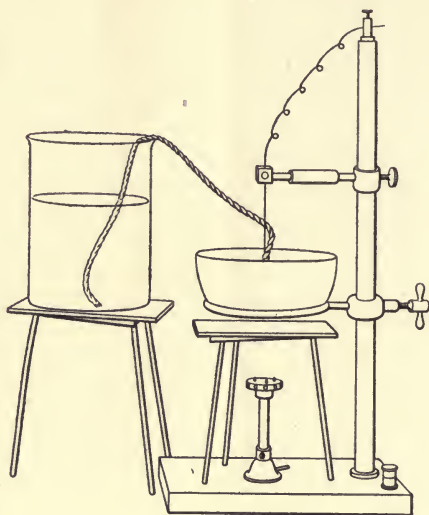


FIG. 12.

evaporation, which results in the exposure of the upper portions of the deposit, which as a result may become oxidised and hence spoiled. To remedy this some liquid must be added as quickly as the loss takes place. Some workers do this by having a burette fixed above the vessel to deliver liquid (usually water) at the necessary rate. Another way is to have a syphon made of cotton wick, which dips into a beaker above the solution. After some little arrangement this in general will give quite satisfactory results (Fig. 12).

The use of electrodes other than platinum has now become fairly common. The most usual variant is the mercury kathode. One form is described under the estimation

of bismuth (*q.v.*). Another good and useful form is that used by Cain (Fig. 13). This consists of a separatory funnel in which the outlet tube is continued inwards for several centimetres. Through the side of the funnel a platinum wire is fixed to give the necessary electrical contacts. The vessel is filled with mercury up to within 2 mm. of the top of the outlet tube, and then the electrolyte poured in above. (The inlet tube may be filled with mercury also, but if this is done, when run out before the solution it should be allowed to drop into a clean beaker, and then returned to the body of the funnel.) The anode is any of the suitable rotatory forms, and is placed quite close to the surface of the mercury. The tap in the outlet tube should have a moderately wide tube so that the liquid may flow out quite quickly during washing, which is generally performed with the current still on. This apparatus gives a fairly large surface area of mercury for only a small weight, better than in the ordinary beaker form. Several other alterations are being attempted by various people, such as the use of amalgamated brass kathodes, or the employment of base metals that have been platinised. None of these appear likely at present to oust the existing arrangements.

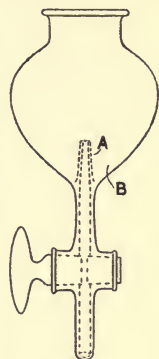


FIG. 13.

A. Exit tube.
B. Platinum tip.

Up to a few years ago the question of potential at the junctions electrode-electrolyte had been neglected very largely in the calculations for electrolytic analysis, but more exact work has resulted in the recognition of the value of this factor. In consequence, the need of some accurate method for the determination of the potential existing at this junction is felt fairly keenly. A very satisfactory arrangement for doing this is the apparatus of Sand, in which he uses a known E.M.F., obtained by tapping off at different points of a rheostat, to balance the E.M.F. set up at the junction kathode-electrolyte, and finds the balance point of the two E.M.F.'s by means of a capillary electrometer. The apparatus and its modifications as introduced by Sand

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has several objects in view. The first is the ready production of a gradation of the potential existing between the kathode and the electrolyte, combined with an easy and continuous measurement of the same. This makes possible various separations of one metal from another by suitable

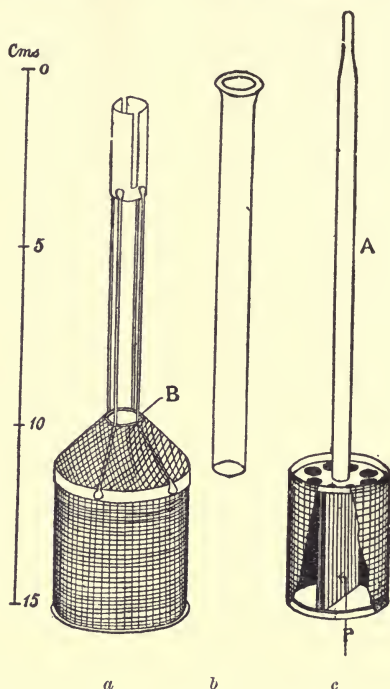


FIG. 14.

a. Outer electrode. *b.* Glass tube. *c.* Inner electrode.
A. Hollow stem. P. Partition.

changes in the value of the potential. The second aim is to reduce the resistance of the electrolyte between the electrodes to the lowest possible value. This brings down the voltage required to drive the current through the electrolyte to the minimum value. Thirdly, the arrangement aims at increasing the velocity with which the ions are brought up to the electrodes. This is accomplished by raising the temperature and by rotating one of the electrodes. In

order to bring about the second object, *i.e.* the reduction of the resistance between the electrodes, Sand designed a pair of electrodes which should work one inside the other, so providing a distance through which the current had to

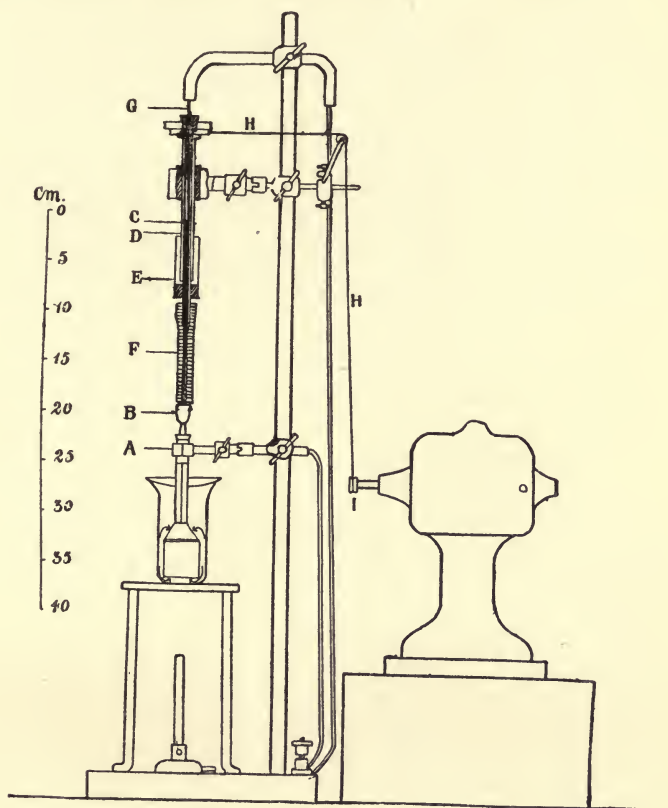


FIG. 15.

- | | |
|-----------------------------------------|---------------------------------------------------------------------------|
| A. Clamp to grip outer electrode. | G. Amalgamated copper wire dipping into the mercury contained in C and F. |
| B. Chuck to grip inner electrode. | H. Cord. |
| C. Glass tube rotating in glass tube D. | I. Pulley of rubber. |
| E. Oil trap on C. | |
| F. Thick rubber tube. | |

be driven of only about three millimetres. These electrodes are shown in Fig. 14. Both are of platinum gauze mounted on rods of either platinum or an alloy of iridium and platinum. The inner one (*b*) is separated from the outer (*a*) by

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a glass tube (c) which holds the hollow platinum-iridium support of the inner electrode. In order to get the maxi-

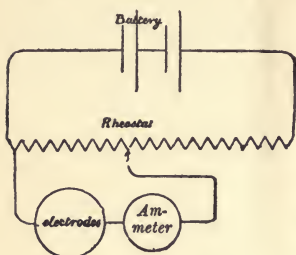


FIG. 16.

imum stirring effect from the electrodes, a glass partition is fixed in the centre of the gauze cylinder. The result is that there is a very intense movement in the space between the electrodes whilst the rest of the solution does not undergo much rotation. The renewal of the solution within the space is produced by a downward current into the

inter-electrode annulus. The electrodes are fixed in position by clamps (Fig. 15). The outer electrode is held in a burette

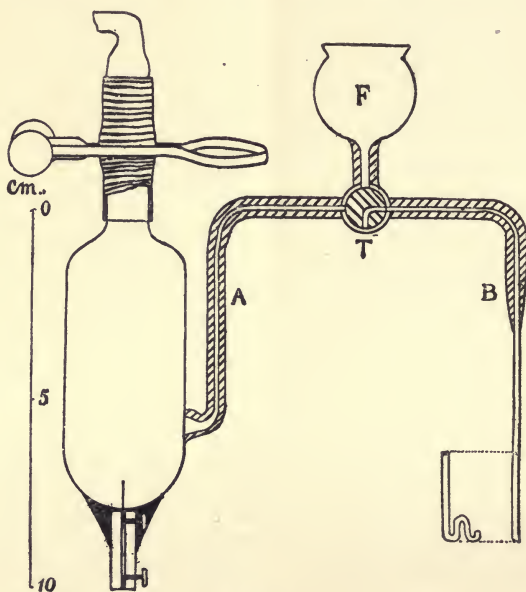


FIG. 17.

A, B. Capillary tube.

T. Three-way tap.

stand in which the cork on the flat side of the clamp has been replaced by a strip of platinum foil. The inner electrode is fixed to a rotating head, an electrical connection being made

by a tube containing mercury. In this way the primary circuit is completed and may be used quite apart from the secondary circuit, which is employed to measure the potential (Fig. 16). The E.M.F. used for this circuit is made variable by the use of a rheostat from which the requisite amount may be taken off.

In the secondary circuit are two sources of potential. One is provided by a cell in circuit with a rheostat enabling any reasonable, variable E.M.F. to be tapped off, this being measured by a delicate voltmeter connected across the terminals from which the tapping is effected. This potential is balanced by that produced by the combination of kathode-electrolyte-normal electrode. This latter (Fig. 17) is a slight improvement upon the ordinary form, care being taken to

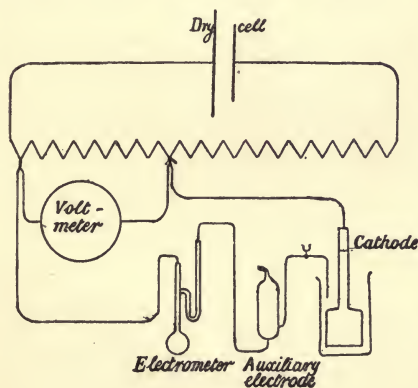


FIG. 19.

prevent diffusion as far as possible. In the exit tube a tap is placed which allows the electrode—i.e. the mercury and mercurous sulphate—to be cut off from the electrolyte in the beaker. The tap is not greased, and in consequence allows a very little of the connecting liquid (sodium sulphate) to slip round the tap and thus make electrical connection. The 2N sulphuric acid, which is the liquid in contact with the mercurous sulphate, is brought up to

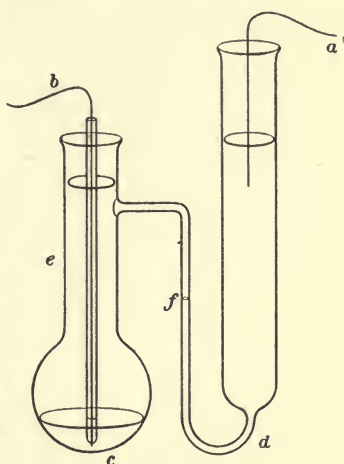


FIG. 18.

- a, b.* Platinum wires.
c, d. Mercury.
e. Dilute sulphuric acid.
f. Observation level of mercury in capillary tube.

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the tap and the sodium sulphate filled from the other side (the tap being a three-way). After each series of measurements a little of the 2N sulphuric acid is forced through the tap to overcome any diffusion that has taken place round the tap. To prevent the diffusive effects at the junction of the sodium sulphate solution and the electrolyte, as far as possible, the end of the tube is bent round several times (Fig. 17). The circuit also contains the capillary electrometer which is used merely as a null instrument, the simplest type being available in consequence (Fig. 18). The secondary circuit is shown in Fig. 19, and this combined with the primary circuit of Fig. 16 represents the whole apparatus. The normal electrode is fixed to a separate stand and may be removed or brought into position at will. With this apparatus many very useful results have been obtained in the direction of the separation of metals whose decomposition voltages are nearly alike, or of those whose values lie near to that of hydrogen.

CHAPTER II

ELECTROLYTIC ANALYSIS

FOR electrolytic analyses on commercial alloys the attention of the chemist is confined to solutions of the metals, and these generally as the ordinary binary compounds of the metals with a simple acid. Occasionally the metal is present in a compound which, when dissolved, does not split up in the ordinary manner giving an ion of the metal, but one containing the metal and another radicle, *e.g.* $[\text{Ag}(\text{CN})_2]'$ or $[\text{Cu}(\text{NH}_3)_2]''$. Usually the problem presented by these solutions may be solved fairly readily by the application of some slight extension of the laws for the binary salts. As is well known, these salts when dissolved in water (or in some few other solvents) are dissociated to a greater or less extent into ions, the degree of dissociation depending upon the concentration and decreasing with an increase in this factor. The ions are supposed to differ from the atoms that were present in the solid substance in several particulars. Firstly, they are endowed with different electrical properties. The ion has a charge of electricity either positive or negative, and in proportion to the valency of the atom from which it has been formed. (The metals if they are free—*i.e.* not in a complex radicle—are all charged relatively positively, whilst the acid radicles— Cl' , SO'' , NO_3' , $(\text{CH}_3.\text{COO})'$ —are negatively charged.) Hence each binary compound splits up into two “substances” having an equal quantity of electricity distributed on each kind, the sign alone being different (*e.g.* NaCl gives $\text{Na}\cdot$ and Cl' , the charges being equal in magnitude—in Na_2SO_4 , the result is $2\text{Na}\cdot + \text{SO}_4''$ —meaning that the charge on the SO_4'' is twice that on each of the $\text{Na}\cdot$). It has been assumed generally that the ion has either one more or one less electron per valence than its parent atom possessed—*e.g.* copper sulphate, CuSO_4 , splits up into two

ions, one Cu^{++} and the other SO_4^{--} , and each of these differs by two electrons from its parent atoms, the SO_4^{--} having two more negative charges and the Cu^{++} having two less. (Since the mass of an electron is only about $\frac{1}{1836}$ of the hydrogen atom it is quite obvious that the difference in properties, other than those influenced by the electrical condition, produced by the presence or absence of the electrons will be fairly negligible.) This means that the ions have some definite charge associated with them, and as a result one should know exactly what electrical charge is to be introduced into the sphere of action within the electrolytic cell by the addition of a known quantity of any metallic salt. This is possible because of the information conveyed by Faraday's Laws.

The first of these laws states that the electro-chemical equivalent of an element is proportional to the ordinary chemical equivalent (that is to say, that the weights of any two metals deposited by the passage of one coulomb of electricity are proportional to their ordinary chemical equivalents). This being so, the possession of the electro-chemical equivalent of any one metal gives those of all the others. The most careful observations have been made with silver solutions, from which it is found that one coulomb deposits 0.0011175 grams of silver. The gram equivalent of silver is 107.93 grams, and hence the quantity of electricity required for the deposition of one gram equivalent of silver is $107.93 \div 0.0011175$ coulombs, *i.e.* about 96,600 coulombs. This is generally spoken of as one Faraday. Obviously by Faraday's Law this same quantity will be required for the deposition of one gram equivalent of any other metal. Consequently one can see well that if there is one gram equivalent of two monovalent metals in two solutions, sufficiently dilute to give all the metal as ions, then there will be the same number of ions in each solution and hence the same charge on each ion in each solution, since by Faraday's Law the quantity of electricity which is supplied at an electrode by the neutralisation of a gram equivalent is the same for any metal.

Another important property of the ions is their velocity. The motion of the ions may be regarded in two senses. First, they have a motion which is comparable with that

of the particles of a gas and which is the basis of the well-known kinetic theory. As a result of this it is possible to conceive the rapid movement of the ions through space more or less filled with other particles, either ions, or undissociated molecules of solute or solvent, and to imagine the innumerable collisions of the particles which are taking place so continuously that the path through which a particle moves between two successive collisions is only very, very short. This conception is of great value for certain purposes, and is the normal state of the electrolytes when the circuit is open. When it is closed and a potential gradient is produced in the circuit from electrode to electrode, these things must change. Within the sphere of influence of this potential gradient are a very large number of particles carrying electrical charges, some relatively positive and some relatively negative. As a result these particles must move, some up and some down the gradient, those possessing the relatively positive charges going down the gradient (*i.e.* from higher to lower potential) and those with the relatively negative charges in the opposite direction. As a result there is a definite convective motion towards the electrodes. This latter convective motion is much more important than the other (*i.e.* the intrinsic, free) motion, in the case of electrolysis, and the various ions have a certain velocity of convection which is peculiar to themselves. It is quite possible to measure these velocities of convection for the various ions, and as they obviously must depend upon the potential gradient it is usual to express the value of the velocity in terms of a fixed value of this gradient—namely, one volt per centimetre, when (to avoid any confusion) the velocity of convection of an ion under the influence of this gradient is termed the mobility of the ion. Some typical mobilities are :

	$\times 10^{-5}$ cm./sec.		$\times 10^{-5}$ cm./sec.
H \cdot . . .	330	OH'	180
Na \cdot . . .	45.2	Cl' . . .	67.8
K \cdot . . .	67.0	Br' . . .	70
NH $_4$ \cdot . . .	66.3	NO $_3$ ' . . .	64
Ag \cdot . . .	56	SO $_4$ " . . .	71
Cu \cdot . . .	49	CH $_3$ COO' . . .	42.1

Evidently in the passage of the current through the electrolyte both ions take part in the carriage of the current, for each ion carries a charge and hence may neutralise a portion of the charge upon the electrode to which it travels, thus lowering the potential of the positive electrode or raising that of the negative one, since it is the particles with a negative charge that go towards the positive electrode and vice versa. Also each monovalent ion has the same charge, and as a result the two actions are equivalent. Further, it will be plain that the quantity of electricity carried (or neutralised at the electrodes—*i.e.* the same thing—this neutralising of charge and consequent change of potential being exactly what is meant by the passage of a current) in any time is proportional to the number of ions moving up to the electrodes in that time, and as the number of ions coming in contact with an electrode is proportional to the velocity of the ion, the current (*i.e.* the quantity \div the time) is proportional to the number of ions present, to their velocities and to their charges. Hence, if α be the degree of dissociation, n the number of gram equivalents of the substance per cubic centimetre, the number of ions will be proportional to $n\alpha$. But a gram equivalent of ions carries a charge of one Faraday, and so if the mobilities of the anions and cations (*i.e.* the negatively and positively charged ions) be U_A and U_C , then the current density will be given by $96,600 n\alpha(U_A + U_C)$ amperes per square centimetre. Evidently this expression represents the conductivity of the solution under a potential gradient between the electrodes of one volt per centimetre. The velocities of the ions are fairly constant whatever the concentration, the variation being slight compared with the alterations of the other factors. The variable factor in the expression is $n\alpha$.

The degree of dissociation α is recognised to be a function of the concentration and may be looked upon from two points of view. The ions in the solution are produced by the dissociation of the molecules of the dissolved substance and are in a state of rapid motion apart from the convective movement towards the electrodes. It is not to be supposed that at any dilution there are always a certain fixed number

of molecules and a certain number of ions each remaining as such, but rather that there is a continuous reversible reaction going on, *e.g.* $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$. The ions are continually combining, dissociating once more and recombining, the process taking place again and again throughout the solution with all the ions and molecules. Hence each ion spends a part of its time in combination and part as dissociated material, and the ratio of the time that it is free to the whole time is one meaning of the term α . Also, as the molecules have no charge of either free positive or free negative electricity they are not affected by the potential gradient, only the ions being subject to this influence. Consequently the convective velocity does not apply to the whole of the dissolved substance, but only to the free parts, and as a result the average convective velocity towards each electrode of the dissolved particles is proportional to the number of ions in the solution. Consequently, if v is the convective velocity of an ion, the average convective velocity of all the similar ions through any time is αv . If U is the actual mobility of an ion in any solution, then αU will represent the effective mobility of this same ion (taken as an average for the whole solution) under the same set of conditions. Either of these two ways of regarding α will serve the same end.

Evidently from what has been said about the continual combination and dissociation, it is likely that anything tending to produce less combination will tend to increase α , and as a greater space for the ions to move decreases the likelihood of meeting another ion for recombination, it is probable that an increased volume (*i.e.* a decreased concentration) will increase α . Hence $k (=96,600 \alpha n(U_A + U_C))$ should be increased in proportion to an increase in α . At the same time the value of n decreases and produces a fall in the value of k . It is found, however, that the product αn is not a constant, but varies, and as a result the value of k does not remain constant with a change in the concentration. In order to give a unit which shall be comparable, and which shall represent as much as possible, a value known as the equivalent conductivity is

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introduced. This is the quotient $k \div n$, *i.e.* the ratio of the conductivity to the concentration. More usually it is expressed as kv , where v is the reciprocal of the concentration, *i.e.* as the number of cubic centimetres of solution containing one gram equivalent of the dissolved substance. Then $kv = \Lambda = 96,600 \alpha(U_A + U_O)$, and evidently as α increases so will Λ . This is found to be true and the

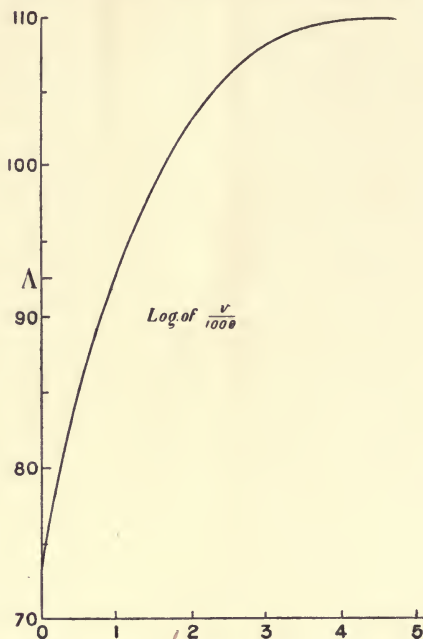


FIG. 20.

values of Λ for any solution are found to increase gradually to a nearly constant value, the curve being asymptotic. The curve given (Fig. 20), contains the values obtained for a solution of sodium chloride, and represents the values of Λ plotted against the logarithm of the reciprocal of n , *i.e.* $\log v$. At great dilutions the value becomes nearly equal to that at infinite dilution, and may be taken as equal without introducing any appreciable error. It is quite safe to assume that this maximum value of Λ is that produced by perfect

ionisation, *i.e.* when the value of a is unity (as the value of U_A and U_o are found not to vary appreciably in the higher dilutions). Evidently, then, this gives a method for the determination of a , it being the ratio of A at a volume v to that at an infinite volume, *i.e.* $a = A_v \div A_\infty$. (It is found that this value of a is almost identical with that obtained by methods depending upon osmotic pressure, &c.) The following are values of A for some solutions :

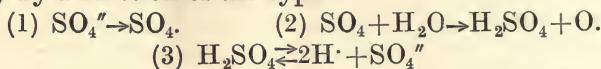
	Gram Equivalent per Litre = 1000 n .			
	0	·0001	·01	·5
KCl	130·1	129·1	122	102
KBr	132·3	131·1	124	105
KNO ₃	126·5	125·5	118	89·2
NaCl	109·0	108·1	102	80·9
AgNO ₃	115·8	115·0	108	77·5
NH ₄ Cl	129·2	122	101
$\frac{1}{2}$ MgCl ₂	109·4	108·9	98·1	69·5
$\frac{1}{2}$ Pb(NO ₃) ₂	120·7	119·9	103	53·2
$\frac{1}{2}$ CuSO ₄	109·9	107·9	71·7	...
HCl	377	376	370	327
HNO ₃	375	374	368	324
$\frac{1}{2}$ H ₂ SO ₄	361	351	308	205
KOH	234	233	228	197

It will be seen from these that the values obtained from A in solutions containing one gram equivalent of the solute in 10,000 litres differ but slightly from those at infinite volume given in the first column.

In the case of the electro-deposition of a metal from a neutral solution, the value of A calculated with respect to the metal must rise somewhat during the progress of the estimation. Its components kv will vary differently. As the metal is removed the value of v will rise whilst that of k will fall, though not in the same proportion. For a will increase and n will fall, but $n = \frac{1}{v}$ and hence A will increase in proportion to the increase of a . As a will vary only between perhaps 0·5 and 1·0 the changes in A are not very great. Those of k , on the other hand, will decrease

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enormously, and so produce a great decrease of kv . As a matter of fact such a case does not exist, since the solution, if neutral at first, is likely to become acid fairly quickly by a reaction of the type



thus increasing the content of $\text{H} \cdot$ ions, and introducing a new factor.

The term Δ may be split up into its two components. If $l_{\text{A}} + l_{\text{O}}$ be the terms applied to $96,600\alpha\text{U}_{\text{A}}$ and $96,600\alpha\text{U}_{\text{O}}$, then $\Delta = l_{\text{A}} + l_{\text{O}}$, and as these terms refer to the separate ions it is usual to call their values for any particular substance in solution the ionic conductivities. They can be calculated readily from a knowledge of Δ , U_{A} and U_{O} . It is more usual to work from the migration ratio of the ion, which for an anion is equal to $\text{U}_{\text{A}} \div (\text{U}_{\text{A}} + \text{U}_{\text{O}})$. Some migration ratios are given below and represent the figures for the anion (*i.e.* of the negatively charged ion) for various dissolved substances. Evidently the value for the cation is $1 - n$ if n is the value for the anion.

Electrolyte.	Migration Ratio of Anion.	Electrolyte.	Migration Ratio of Anion.	Electrolyte.	Migration Ratio of Anion.
KCl . .	0.505	AgNO ₃ .	0.526	HCl . .	0.159
KBr . .	0.504	NH ₄ Cl ₂ .	0.507	HNO ₃ .	0.17
KNO ₃ .	0.497	CaCl ₂ . .	0.562	H ₂ SO ₄ .	0.17
NaCl . .	0.604	BaCl ₂ . .	0.55	KOH . .	0.74
NaNO ₃ .	0.629	ZnSO ₄ . .	0.64	NaOH . .	0.8
LiCl . .	0.67	CuSO ₄ . .	0.625		

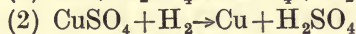
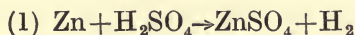
This ratio represents the proportion of the current carried by the anion, and hence the anionic conductivity will be equal to this value multiplied by the equivalent conductivity of the solution. In this way an estimation of the ionic conductivities may be obtained, and it is found that these values are very nearly constant for almost any simple combination of anions and cations. As a result the equivalent conductivity of any solution can be determined by the

addition of the conductivities of the constituent ions. The following are the values at infinite dilution for the conductivity of some ions, the values for smaller dilution being less, as is to be expected :

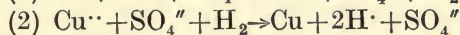
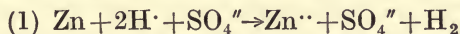
Li . . .	33.44	$\frac{1}{2}$ Zn . . .	45.6	$\frac{1}{2}$ SO ₄ . . .	68.7
Na . . .	43.55	$\frac{1}{2}$ Mg . . .	46.0	Cl . . .	65.44
K . . .	64.67	$\frac{1}{2}$ Ba . . .	56.3	Br . . .	67.63
NH ₄ . . .	54.4	$\frac{1}{2}$ Pb . . .	61.5	NO ₃ . . .	61.78
Ag . . .	54.02			CH ₃ COO . . .	35.00
H . . .	318.0			OH . . .	174.00

If l_A or l_C be known by any means (generally by the migration ratio determined in a manner apart from a knowledge of U_A or U_O) the effective mobility of the ion may be determined, since $\frac{l_A}{96,600} = aU_A$. The values obtained thus are found to agree closely with those obtained in practice.

This brief account shows in some measure what happens in the electrolytic solution whilst the current is flowing, but it will have been noticed that everything depends upon the establishment of a definite potential gradient between the two electrodes. The production of this is referred to in the account of apparatus, but only as to the question of the external arrangements required for it. One of the principal sources of E.M.F. (and, in fact, the usual one for the kinds of current used in electrolysis) is the voltaic cell. This is merely a machine for the transformation of chemical energy into electrical energy *via* chemical reaction and the heat effects attendant upon it. This is exemplified in the Daniell cell. In this case the two principal chemical reactions are :



Expressed in terms of their ions they will be seen to be



Evidently in the case of (1) the zinc has received some electrical charge (or has lost some—according to convention)

by the passage from the metallic (*i.e.* atomic) to the ionic condition, and similarly the copper has lost some (or gained some) by the change from the ionic to the metallic state. For convention, assume that the zinc in passing from the atomic to the ionic state has lost two negative charges and that the copper, in the reverse process, has gained two, thus making the zinc plate relatively more negative and the copper plate relatively more positive. These changes do not require exactly the same quantity of energy—a different number of ergs being produced in the solution of one gram equivalent of copper than in the solution of one gram equivalent of zinc. This difference is the cause of the electrical energy of the cell, and evidently is due in a great measure to the formation of ions by the metal. It is in fact attributable directly to the fact that the various metals have different tendencies to pass into the ionic state. The E.M.F. of the cell is in some degree a measure of the work done in these particular transformations. In the case of the cell above, the order of formation of ions is evidently Zn^{++} , H^+ , Cu^{++} , and a list of metals can be drawn up on this basis, the order being slightly different under various conditions. A fairly representative order, going from those with the greatest tendency to form ions, is Mg, Al, Mn, Zn, Cd, Tl, Fe, Co, Ni, Pb, Sn, H, Bi, As, Sb, Cu, Hg, Ag, Pd, Pt, Au.

It is evident from the above that it is possible that the solution and the metal in any one case may be at quite different potentials, for in the case of the zinc passing into the solution, the Zn^{++} ions have a (relatively) positive charge (*i.e.* have been depleted of part of their negative) and as a result leave the metal (relatively) negative. In consequence an electrical double layer is formed at the surface of the metal. Exactly the opposite occurs in the case of the copper. If the zinc is going into solution in acids this goes on till the zinc is used up, and no useful work is done, but if the other pole, *i.e.* the copper plate, be connected then work may be extracted from the combination. It is more useful to consider the question of potential for those cases in which a metal is placed in contact with a solution containing its

own ions ; for the Daniell cell, after the solution of even the smallest weight of zinc, becomes similar to this, and this condition of a metal against its own ions is normal in the ordinary electrolytic cell during an action. In this case there are two forces at work. The first of these is that tendency, spoken of above, that the metal possesses for going into the ionic state. It has been said that this varies with the metal, and may be taken as a constant for any one metal. This tendency to form ions has been likened by Nernst to an ordinary fluid pressure, and he terms it the electrolytic solution pressure of the metal. The other force is one which exists in any and every aqueous solution, and is associated with the tendency of ions to come out of solution manifested by the ordinary phenomenon of the desire to increase the volume of the solution, and is, of course, the osmotic pressure. These two forces act in opposite directions, the one tending to make ions from atoms, and the other to produce atoms from ions. Evidently, if in a solution these are exactly equal, there will be no change at all in the electrical condition. On the other hand, if the solution pressure is greater than the osmotic pressure, then there will be a passage of more ions into the solution. This will mean that the solution will be at a higher potential than the metal. On the other hand, if the osmotic pressure is higher than the solution pressure, some of the ions will come out of the solution and form on the metal, thus giving the solution a different potential from the metal. By equating thermodynamically the work done in certain of these ideal cases, it is possible to arrive at an expression for the potential difference set up between the metal and the solution under these circumstances, and the Nernst formula for these data is

$$E = \frac{RT}{rF} \log_e \frac{P}{p}$$

in which P =the electrolytic solution pressure, p =the osmotic pressure of the solution, R =the gas constant expressed in volts \times coulombs, T =the absolute temperature of the solution, r =the valency of the ions sent out or taken in, and F =one Faraday=96,600 coulombs. For F and R

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the numerical values can be substituted, and the natural logarithms can be converted into common logarithms by dividing by the factor 0.4343. Also T can be assumed at some general value (*e.g.* 18°C.), and this also substituted in the formula, which then becomes

$$E = \frac{8.316 \times 291}{r \cdot 96,600} \times \frac{1}{0.4343} \times \log_{10} \frac{P}{p} \text{ volts}$$

$$= \frac{0.058}{r} \log \frac{P}{p} \text{ volts.}$$

This represents the single electrode potential in any combination of metal-solution, and it is by combining two of these that the ordinary voltaic cells are built up. The formula must act in the case of the electrolytic cell. Here there is an immediate production of an electrode of the type, metal against solution of its ions when the metal is deposited upon the platinum, the E.M.F. being in the direction tending to send a current contrary to that of the electrolysing current which is passing through the cell. The electrolysing current in consequence must supply some potential difference at the electrode sufficient to overcome this in addition to doing the other work of the cell—due to Ohm's Law resistance, &c. Evidently, too, this E.M.F. is the minimum that must be applied at the junction (*i.e.* the electrode) by the current in order to deposit any metal at all from the solution.

In the ordinary electrolytic cell the effect at the other electrode—the anode usually—must be added, the decomposition voltage of the solution being the sum of the minimum E.M.F. required to deposit kations at the kathode and anions at the anode. During an electrolysis there will be an alteration of potential at the two electrodes, due to the change in concentration of the solution which is reflected in the variation in the osmotic pressure. When brought to show the effect of changes in concentration, the Nernst formula becomes

$E = E_0 + \frac{0.058}{r} \log C$, where E_0 is the electro-affinity of the combination, and C is the concentration in gram-equivalents per litre of the ion given off. This is the electrode potential

in the case when the solution is normal (*i.e.* 1 gram-equivalent per litre) with respect to the *ion* given off by the metal (note that a normal ionic solution is not a normal solution of the substance containing the atom from which the ion is produced—because of the influence of the degree of dissociation α). Some values of the electro-affinity are :

Zn . . .	-0.493	Hg . . .	+1.027
Cd . . .	-0.143	Ag . . .	+1.048
Fe . . .	-0.063	I . . .	+0.797
Co . . .	+0.045	Br . . .	+1.270
Ni . . .	+0.049	O . . .	+1.396
Pb . . .	+0.129	Cl . . .	+1.694
H . . .	+0.277	NO ₃ . .	+1.75
Cu . . .	+0.606	SO ₄ . .	+1.9

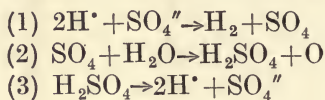
(The sign refers to the relation of electrode and solution—the electro-affinity being positive when the electrode is positive with respect to a normal solution of its ion.)

The formula shows that if the solution is dilute, a change of concentration of tenfold will cause a change of potential of 0.058 volts for a univalent ion, 0.029 for a divalent and 0.0193 for a trivalent ion. Evidently the potential difference at an electrode at which a kation is depositing becomes greater as the concentration is lowered, and as the concentration is finally reduced to nearly zero, the potential difference must become very high. It will be seen, however, that when the concentration is reduced to $\frac{1}{10,000}$ of its original (*i.e.* to the limit of most chemical tests), the potential difference has only been increased by 0.232 volts if a monovalent ion is being considered. As a result there is not likely to be any unwieldy change in the decomposition voltage at the electrodes. Also, whilst the potential of one electrode may be rising, that of the other may fall, so helping to keep the total potential drop of the cell fairly constant.

It is important, however, that one other reaction should be taken into account. It has been assumed above that no particular pair of substances which may be liberated at the electrodes are exempt from the rules stated, and as a result the decomposition of such diverse substances as strong acids,

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various metallic salts, and the hydroxide of alkali metals, in solution, all obey the same laws. The case of the acids presents at least one feature of importance. In the case of an acid such as sulphuric, the reactions are :



The products of the electrolysis are hydrogen and oxygen, these being produced at different electrodes and as a result will dissolve in the metals of the electrode to a certain extent. Consequently, they will exert the back E.M.F. described above. Evidently there will be a decomposition voltage for this solution just as for any other, and will be (according to the table given above) $1.396 - 0.277 = 1.12$ volts. This is the E.M.F. that can be got out of the combination, and as a result the application of any E.M.F. greater than this should result in the continual decomposition of the solution. In practice it is found that this is not so—that a greater E.M.F. must be applied, and that the value of this is dependent to a great extent upon the nature of the surface at which the two gases are allowed to separate. The value required for platinised platinum electrodes is 1.475 volts, whilst in the case of polished platinum it is 1.79 volts. This raising of the decomposition voltage is referred to as over-voltage and is a fairly constant value for any particular surface. It is important in various cases of electrolysis. Suppose that a solution contains several ions which may be deposited at the kathode. Evidently these might be supposed to be deposited together or selectively. What happens is that the one whose separation involves the least expenditure of work—*i.e.* the one with the highest electro-affinity, according to the convention of p. 31, will go out first. This tendency to deposit is the predominating factor, but other things come in. First of all, the number of each of the ions present has a great influence (*cf.* the osmotic pressure), as it is reflected in the decomposition potential of the ion. As a result the passage of the current may increase the potential of the electrode with

reference to the first ion to such a degree that the deposition of the second ion is just as easy, and then both go out of solution together. If hydrogen was the alternative ion, and it obeyed the rule (without any over-voltage effects), its separation would take place much more easily than that of many other metals. In view of the existence of the over-voltage, the separation of hydrogen very often does not take place, the deposition of the metal taking place in preference, although the hydrogen ions are present in much greater quantities. This variation is of great use in effecting separations. If the potential drop at the kathode is kept at a certain value, above that required for the discharge of one set of ions and below that required for another set of ions, there will be a perfect separation. As has been said above, after a time the decomposition voltage at the kathode of any metallic ion may rise owing to a fall in the concentration, and this may result in the production of such conditions that a further separation is not possible.

CHAPTER III

PRECIPITATIONS BY MEANS OF HYDROGEN SULPHIDE

MOST of the metals occurring in commercial alloys can be precipitated as sulphides from solutions of their salts; the customary qualitative separation of the so-called "heavy" metals from the metals of the "iron group," *e.g.*, is based upon the use of hydrogen sulphide, which completely precipitates the sulphides of the former group and not those of the latter, from solutions containing free hydrochloric acid. Moreover, there are great variations in the behaviour of the sulphides of the first group; temperature of precipitation, concentration of the solution with respect to the metal, and degree of acidity are factors which operate differently in different cases, and determine not only the completeness or incompleteness of the precipitation, but to some extent also the physical condition of the separated sulphide. Thus it is a well-known fact that arsenic can be completely precipitated as sulphide from solutions, the acid concentration of which is great enough to retain the allied metals in perfect solution. Clark's¹ separation of antimony from tin is based upon the insolubility of antimony sulphide in concentrated oxalic acid solution, that of Panajotow² upon the use of a 15 per cent. solution of hydrochloric acid, whilst Vortmann and Metzl³ use phosphoric acid for the same purpose. The relative stability of metallic sulphides towards hydrochloric acid has been made the subject of investigation by various observers from time to time. As long ago as 1838, *e.g.*, Reimsch⁴ mentions that lead is not

¹ *Chemical News*, xxi. 124.

² *Berichte*, xlii. (1), 1496.

³ *Zeit. Anal. Chem.*, xlv. 525.

⁴ *Journ. f. pr. Chemie*, xiii. 129.

precipitated by sulphuretted hydrogen from solutions of a certain degree of acidity, and that it can thus be separated from small amounts of such metals as arsenic, silver, copper, antimony, &c., which are completely precipitated under similar conditions. He arranges the sulphides in the following order with respect to their solubility in hydrochloric acid:—As, Ag, Cu, Sb, Bi, Hg, Au, Pb, Pt, Sn, Zn, Fe, (Ni, Co, Mn). Similarly Martin¹ observed that, besides lead and antimony, such metals as silver, copper, bismuth, tin, mercury, and cadmium are not precipitated by sulphuretted hydrogen at acid concentrations which permit the precipitation of gold, platinum, and arsenic, and he gives the following arrangement of the metals:—Ag, Cu, Bi, Hg, Sn, Sb, Cd, Pb.

More precise information on this subject is now available owing to the exhaustive work of modern investigators. The Panajotow separation of antimony from tin dates to 1909, and most of the metals which constitute the essential constituents of non-ferrous alloys have been systematically investigated during the last decade with respect to the precipitation of their sulphides from solutions containing free hydrochloric acid. A concise account of the most important results is subjoined.

Copper.—The case of this metal was taken in hand by Strell,² and the following table embodies the results. In every test (a) the volume of the copper solution was 100 c.c., (b) the concentration with respect to copper was decinormal, and (c) hydrogen sulphide was passed briskly for 30 minutes. Constancy of concentration was maintained at temperatures above 50° C. by the addition of water in precipitating from solutions of less than 6N acid. In the case of the precipitation from 6N acid solutions, acid of that strength was added to maintain constant volume, all such additions being made at the temperature of precipitation. The figures in the table are the number of milligrams of copper oxide

¹ *Journ. f. pr. Chemie*, lxxvii. 371.

² *Diss.*, München, 1908.

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recovered from the filtrates in cases of incomplete precipitation :

Concentration of HCl.	Temperature of Precipitation.								
	20°	30°	40°	50°	60°	70°	80°	90°	Boiling Point.
N
2N	0.6
3N	0.1	0.4	0.6	7.0
4N	0.2	0.2	0.3	0.6	1.1	25.3
5N	0.2	0.3	0.3	0.5	0.9	1.5	2.7	6.9	47.6
6N	0.5	1.0	4.3	5.1	16.3	37.0	52.9	182.4	Copper completely in solution.

Complete precipitation of the copper is marked off from incomplete precipitation by the thickened line, and the following conclusions can at once be drawn :

- (1) Copper is quantitatively precipitated at all temperatures from solutions containing hydrochloric acid of normal strength, and nearly so from solutions of twice that strength of acid.
- (2) Precipitation is complete up to 60° from 3N acid solutions, and up to 40° from 4N acid solutions, whilst absolutely complete precipitation is impossible under ordinary working conditions of temperature from solutions of 5N and 6N hydrochloric acid.

The significance of these results is referred to below.

Lead.—The conditions determining the complete precipitation of lead were also investigated by Strell (*loc. cit.*). In this case the concentration with respect to lead was

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$\frac{1}{50}$ N, the other conditions remaining the same, viz. 100 c.c. of solution, and hydrogen sulphide briskly bubbled through the solution for half an hour. The sparing solubility of lead chloride in aqueous or acid solution constitutes another factor in this case of which notice is made in the subjoined table, the figures in which represent the number of milligrams of lead sulphate recovered from the filtrates in each case.

Concentration of Hydro- chloric Acid.	Temperatures of Precipitation.				
	20°	40°	60°	80°	Boiling Point.
nil
$\frac{N}{10}$	0·6 0·2	6·0 4·9
$\frac{N}{4}$	Separation of lead chloride	4·4 3·5	58·7 60·3
$\frac{N}{2}$	do.	...	6·6 5·9	61·3 63·4	All lead in solution
$\frac{3N}{4}$	do.	2·0 3·2	43·5 45·1	198·8 191·3	All lead in solution
N	do.	13·6 15·3	136·2 130·0	All lead in solution	
2N	Separation of lead chloride		Lead completely in solution		

It follows from the table that

- (1) Precipitation from an aqueous solution of lead chloride is perfect at all temperatures from 20° up to the boiling point.

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(2) Precipitation of lead sulphide is perfect up to 60° from $\frac{N}{10}$ and $\frac{N}{4}$ acid solutions, and up to 40° from $\frac{N}{2}$ solutions.

(3) Lead chloride separates from $\frac{N}{4}$, $\frac{N}{2}$, $\frac{3N}{4}$ and N acid solutions at 20°, and from 2N solutions at 40°.

(4) Lead remains entirely in solution at 60° and upwards in the case of 2N acid solution, and at 80° and upwards in N solutions.

Before proceeding to the cases of other metals, a brief consideration of the two preceding ones may be profitable. Supposing, for example, the necessity arose of separating an approximately known amount of lead from another metal whose sulphide was more stable towards hydrochloric acid; it is seen from the table that at a temperature of, say 60°, and from solutions containing normal hydrochloric acid, hydrogen sulphide fails to precipitate the equivalent of 130 milligrams of lead sulphate from 100 c.c. of an $\frac{N}{50}$ solution of that metal. Obviously, therefore, by doubling the volume and maintaining other conditions the same, the lead may be retained in complete solution. To take the specific case of the two metals just dealt with, which so frequently occur together in alloys, a comparison of the tables shows that copper can be completely precipitated at all temperatures from N acid solutions and up to 90° for 2N acid, whereas lead is completely retained in solution from 80° up to boiling point in N acid, and from 60° in 2N acid. The differences are sufficiently large to admit of a quantitative separation, and test analyses prove that the separation can be readily accomplished. By precipitating from binormal hydrochloric acid solutions at 80° C., replacing loss by evaporation from time to time, the copper was completely recovered from several test mixtures of that element with lead of $\frac{N}{50}$ concentration. The precipitated copper sulphide was collected and washed with 2N hydrochloric acid satu-

rated at 80° with sulphuretted hydrogen, and the whole of the lead obtained from the filtrate. Strell gives test analyses which show the accuracy of the separation in cases varying from a mixture of 250 milligrams of copper with 200 of lead to one of 65 of copper with as much as 800 of lead.

Antimony.—The precipitation of antimony as sulphide and the subsequent determination in that form constitute one of the best methods of assaying the element (see p. 91). Hydrogen sulphide precipitates from trivalent and pentavalent antimony solutions. The trisulphide exists in two modifications, an amorphous red and a black crystalline variety. Both are obtainable from antimonious solutions by means of hydrogen sulphide, the first effect of which is to produce the red variety. The change from the red to the black crystalline sulphide is conditioned by the temperature of precipitation and the degree of acidity of the solution. At low temperatures the amorphous red compound is obtained from solutions of any degree of acidity up to 5N strength, which marks the limit of complete precipitation at 0° . As the temperature rises the colour of the precipitate changes, passing through various shades of dark red until finally the black crystalline sulphide is obtained. These changes in colour, accompanied by a marked diminution in volume, are more readily brought about in strong than in weak acid solutions; thus, whilst the precipitates obtained from normal hydrochloric acid solutions are red and voluminous at all temperatures up to the boiling point, the black variety is obtained between 80° and 100° from 2N solutions, and between 60° and 80° from 3N solutions.

For purposes of subsequent manipulation, it is obviously an advantage to secure the black sulphide, but to do so may involve incomplete precipitation of the metal unless due regard is paid to the solubility of the sulphide in hydrochloric acid. The proper choice of conditions, when the determination of the metal in this form is contemplated, becomes therefore a matter of some importance, and is dealt with on p. 92.

From pentavalent antimony solutions hydrogen sulphide throws down an orange-red precipitate, which consists at first principally of antimony pentasulphide. Reduction

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takes place also, however, and in general a mixture of sulphur with tri- and pentasulphide is obtained. In this case also under suitable conditions of temperature and acidity, the change to the black trisulphide can be induced.

The conditions governing the complete precipitation of antimony from trivalent solutions were exhaustively investigated by Scharrer,¹ whose results are reproduced in the following table. In each test 100 c.c. of a decinormal antimony chloride solution were taken, and a rapid stream

Concentration of Hydrochloric Acid.	Temperatures of Precipitation.					
	0°	20°	40°	60°	80°	Boiling Point.
N	Nil	Nil	Nil	Nil	Nil	Nil
2N	Nil	Nil	Nil	Nil	Nil	0.6 0.8
3N	Nil	Nil	Nil	Trace	1.3 2.0	9.4 11.1
4N	Nil	Nil	0.4 0.6	1.6 1.8	10.6 12.9	No ppte.
5N	Nil	1.0 1.6	6.9 7.6	71.2 74.5	No ppte.	No ppte.
6N	1.6 2.4	24.2 27.1	291.5 312.9	No ppte.	No ppte.	No ppte.
7N	Ppte. impossible of filtration.	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.
8N	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.

¹ *Diss.*, München, 1911.

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of sulphuretted hydrogen passed through. The rate at which the gas is delivered (in this case 1 litre per minute) is not entirely without influence on the precipitation both as regards completeness and physical properties of the sulphide. The figures in the table are the amounts of antimony tetroxide, in which form the element was determined, recovered from the filtrates in cases of incomplete precipitation.

The following table shows the results obtained by passing a much slower current of hydrogen sulphide, viz. 12 to 15 c.c. per minute. In both series of tests the gas was passed for an hour.

Concentration of Hydrochloric Acid.	Temperatures of Precipitation.					
	0°	20°	40°	60°	80°	Boiling Point.
N	Nil	Nil	Nil	Nil	Nil	2.2 2.9
2N	Nil	Nil	Nil	Nil	0.5 0.8	93.4 97.1
3N	Nil	Nil	Nil	0.6 0.8	12.0 15.8	No ppte.
4N	Nil	Nil	2.2 1.8	7.2 9.1	123.2 140.7	No ppte.
5N	Nil	4.0 4.9	23.9 20.1	165.5 171.2	No ppte.	No ppte.
6N	6.7 5.8	87.1 92.8	431.8 478.0	No ppte.	No ppte.	No ppte.
7N	Ppte. impossible of filtration.	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.
8N	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.

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Tin.—This metal can be precipitated completely from acidified stannous, as well as from stannic solutions, by means of hydrogen sulphide. Stannous sulphide, so obtained, possesses a dark-brown colour, and is not so stable towards hydrochloric acid as the yellow stannic sulphide. It differs from the latter also by being almost insoluble in alkaline monosulphides, which are so frequently used in the separation of sulphides of arsenic, antimony and tin from those of lead and copper. As, moreover, the methods of opening out white metal alloys generally result in the production of quadrivalent tin solutions, the conditions determining the precipitation of stannous sulphide need not be considered.

Sulphuretted hydrogen effects no reduction of stannic solutions, and in this respect the metal differs from antimony and arsenic.

Scharrer (*loc. cit.*) has investigated the conditions governing the precipitation of stannic sulphide and the results are reproduced in the following tables. As in the case of antimony, 100 c.c. of a decinormal stannic chloride solution

Concentration of Hydrochloric Acid.	Temperatures of Precipitation.					
	0°	20°	40°	60°	80°	Boiling Point.
N	Nil	Nil	Nil	Nil	Nil	1·6 1·4
2N	Nil	Nil	Nil	Trace	18·4 17·2	378·1 377·7
3N	Nil	Trace	13·3 12·7	270·2 259·9	378·4 378·2	No ppte.
4N	Filtration impossible.	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.
5N	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.

Concen- tration of Hydrochloric Acid.	Temperatures of Precipitation.					
	0°	20°	40°	60°	80°	Boiling Point.
N	Nil	Nil	Nil	Trace	234·8 221·5	No ppte.
2N	Nil	Nil	122·4 129·3	316·4 309·1	No ppte.	No ppte.
3N	33·4 31·7	221·9 232·7	No ppte.	No ppte.	No ppte.	No ppte.
4N	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.	No ppte.

were used in each test, hydrogen sulphide was bubbled for an hour, in the first series of tests at the rate of a litre per minute and in the second at from 12 to 15 c.c. per minute. The figures are milligrams of stannic oxide recovered from the filtrates.

A comparison of these tables with the corresponding ones for antimony leads to some interesting conclusions. In the first place it is at once evident that stannic sulphide is much more soluble in hydrochloric acid than antimony trisulphide, and this fact, as already pointed out, makes it possible to effect a separation of the two metals by means of sulphuretted hydrogen. Secondly, the rate of delivery of the gas through the solutions is a matter of the greatest importance in the case of tin, and is not without influence on the precipitation of antimony. To this may doubtless be ascribed the contradictory results obtained by various observers in attempting the separation of the two metals.

With regard to this matter, a closer examination of the tables shows that the separation is possible under the following different conditions :

- (1) Precipitation from 3N acid solutions at 40° by means of a slow current of hydrogen sulphide.

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(2) Precipitation from 4N acid solutions at 20°.

(3) Precipitation from 5N acid solutions at 0°.

As the second and third of these are not influenced by the speed of the gas current, and as the temperature in the third case introduces slight difficulties in manipulation, it is obvious that the second method is the best. The conditions in this case are almost exactly those specified by Panajotow, as 15 per cent. acid has very nearly four times normal strength.

Arsenic.—Hydrogen sulphide precipitates a yellow trisulphide from trivalent arsenic solutions in the cold, and at once if hydrochloric acid is present. From pentavalent solutions no precipitate forms at first in cold solutions; usually a slow oxidation of the sulphuretted hydrogen takes place with the usual separation of sulphur, and this is followed by a precipitate of the trisulphide. At the same time more or less pentasulphide of arsenic is precipitated, so that the final product is generally a mixture of sulphur with tri- and pentasulphide of arsenic. At certain acid concentrations the reduction of arsenic solutions does not take place and the precipitate consists, therefore, entirely of pentasulphide. The influence of acid on the formation of the pentasulphide has been studied by Usher and Travers,¹ and by Brauner and Tomicek.² The latter observers find that from an arsenic acid solution of 0·366 per cent. strength, hydrogen sulphide precipitates at 15° C.

* 91 per cent. As_2S_5 at a concentration of 1·8 per cent. HCl

pure	„	„	„	7·9	„	„
pure	„	„	„	10·76	„	„
pure	„	„	„	14·34	„	„
58 per cent.	„	„	„	20·10	„	„
pure	„	„	„	32·27	„	„

Whatever the composition of the precipitate may be, the amount of free hydrochloric acid is without influence on the completeness of the precipitation—arsenic is precipitated completely from its solutions at all acid strengths by

¹ *Journ. Chem. Soc.*, 87 (1905), 1370.

² *Monatsch. f. Chem.*, 8 (1887), 607.

means of sulphuretted hydrogen. The determination of the element in the form of sulphide is dealt with on p. 116.

Zinc.—Zinc is usually classified with manganese, iron, nickel and cobalt, the sulphides of which are not precipitated from solutions containing free hydrochloric acid. Sulphide of zinc can be precipitated, however, from solutions which are distinctly acid, and the metal in this respect constitutes a sort of connecting link between the “heavy” metals and those of the “iron group.” It is well known, *e.g.*, that comparatively large quantities of such organic acids as formic, acetic, citric, succinic and chloracetic fail to arrest the precipitation of zinc by hydrogen sulphide, and several processes for the separation of zinc from nickel, manganese, &c., are based upon this fact. These acids are generally introduced in the form of their ammonium or sodium salts, which, by interaction with any free mineral acid present at first, or generated by passing the gas, substitute the organic acid in the solution. The precipitation of zinc in this manner is invariably complete, given sufficient time, but there is liability to contamination by small quantities of the allied metals, and notably nickel or cobalt.

It is by no means impossible, however, to effect a nearly perfect precipitation of zinc sulphide from solutions containing free hydrochloric acid or free sulphuric acid, provided that a neutral salt of ammonium or potassium is introduced in considerable amount. For this purpose ammonium chloride, sulphate, and thiocyanate are frequently used; these function simply as “salting-out” agents. Vestner¹ finds that almost complete precipitation of zinc as sulphide takes place under the following sets of conditions:

	Sulphate Solutions.	Chloride Solutions.
Time of precipitation . . .	One hour	One hour
Concentration of zinc . . .	$\frac{1}{10}$ normal	$\frac{1}{30}$ normal
Concentration of acid . . .	$\frac{1}{100}$ N sulphuric	$\frac{1}{300}$ N hydrochloric
Concentration of ammonium salt	Normal sulphate	$\frac{1}{10}$ N chloride

¹ *Diss.*, München, 1909.

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From solutions of manganese, iron, nickel and cobalt, the degree of acidity of which was as little as one-thousandth normal hydrochloric acid, he failed to obtain a precipitate, and from sulphate solutions of the same acidity only cobalt yielded a precipitate weighing about two milligrams.

CHAPTER IV

LEAD

MOST of the commercial engineering alloys contain lead in greater or less quantity. The purer brasses hold less than 1 per cent., whilst the lead contents of the softer white metals reach nearly 90 per cent., and "hard lead," a well-known commercial material, may contain as much as 98 per cent. Evidently, therefore, the methods required for the successful estimation of lead in these various materials must vary considerably, and methods which may be quite suitable for a white metal would fail signally if applied to a brass.

The historic methods for the estimation of lead are naturally gravimetric. The first is the separation and estimation as sulphide, from solutions in which the copper has been fixed, and the second the estimation as sulphate. These two still constitute the skeleton of various others. The sulphide method has been rendered more accurate by the solution of the precipitate in nitric acid, followed by evaporation to fumes with sulphuric acid. The resulting lead sulphate is collected on a weighed Gooch crucible and ignited at a low red heat. The sulphate process is still used as such, the precipitate being treated as just described. It is also quite common to dissolve the lead sulphate in ammonium acetate and precipitate the lead from the resulting solution as a molybdate. The latter procedure, if followed by a re-precipitation, is probably as accurate as any other proposed method for the determination of lead.

The modern methods of determining lead in pure solutions fall naturally into three classes—gravimetric, volumetric and electrolytic.

Amongst the gravimetric one of the neatest, as well as one of the most accurate procedures, for a solution containing

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comparatively large amounts of lead, consists in evaporating the chloride solution over a water bath to dryness, moistening the residue with one or two drops only of hydrochloric acid, and extracting with absolute alcohol, in which lead chloride remains insoluble. The crystals of lead chloride may be conveniently collected on a Gooch crucible and dried at 100°C .

The molybdate process, *i.e.* precipitation as lead molybdate from acetic acid solution without previous separation as sulphate, is very much used. Here the chief disadvantage lies in the uncertain composition of the precipitate if the quantity of lead be large. This difficulty can be overcome by re-precipitation.

Other methods are the precipitation as chromate from acetic acid solution, the precipitation as oxalate from similar solution, precipitation with stannous chloride from an alkaline solution, and precipitation with ammonium persulphate.

The electrolytic processes show less variety, the most useful and valuable being the estimation as peroxide, obtained by precipitation on the anode from a solution containing a considerable percentage of nitric acid. This estimation is not interfered with by most metals (manganese being an exception) and can be carried out very suitably along with the deposition of copper. Much work has been done by Hollard and others to show that the precipitate is not accurately PbO_2 but contains a definite quantity of impurity which reduces the lead factor from 0.866 to 0.853. Considerable care must be exercised in this method to ensure the production of a deposit which will adhere satisfactorily to the electrode. For large quantities of lead a gauze electrode is all but essential, and rotation a help. A method has been devised by Snowden¹ to deposit the metal as such on the very rapidly rotating cathode from solutions containing free acetic acid. In view of the rather doubtful advantages claimed for this method over the peroxide deposition, it is hardly likely to find favour.

¹ *Journ. Phys. Chem.* (1906), 10, 500.

The various volumetric methods in use have almost the same objectionable features. In practically every one the nature of the process renders the result only approximate. If solutions of a strength suitable for use with large amounts of lead are employed, then an error of 0.1 c.c. in the titration means an error of perhaps 0.3 or 0.4 per cent. in the result. If the quantities of lead are reduced, and concomitant variations made in the strength of the standard solutions, this difficulty is overcome in part, but another arises at once in the form of the almost insuperable difficulties connected with the preparation of the pure lead solutions from the alloy. As rapid checks the volumetric processes are valuable, but they are never likely to replace the gravimetric.

Among the best known methods is the titration of the lead in acetic acid solution with a standard solution of ammonium molybdate, using as indicator the brown colouration produced by tannin and the molybdate. This process requires an allowance to be made for the volume of ammonium molybdate required to give the colour reaction with the indicator, the amount of such allowance depending upon the volume of the liquid.¹

An equally suitable and convenient method is that of precipitating the lead as chromate by means of a standard solution of potassium dichromate, the latter being added to the boiling acetic acid solution of the lead from a burette. The end point is partly indicated by the behaviour of the precipitate, which falls down rapidly, after swirling, just before the end of the reaction. The exact end point is determined by means of an external indicator in the form of silver nitrate.

Another interesting process is that of titrating the lead in a solution made strongly alkaline with caustic soda with potassium permanganate, the lead equivalent of which has been determined empirically.² This presents no advantages over the two previous methods.

Details of an iodimetric method have been worked out

¹ Sacher, *Chem. Zeit.* (1909), 33, 1257.

² Bollembach, *Zeit. anal. Chem.* (1907), 46, 582, and *Chem. Zeit.* (1909), 33, 1142.

by Cervi,¹ who uses the dichromate precipitation, and titrates an aliquot portion of the filtrate obtained after the removal of the lead chromate with an excess of potassium iodide, the liberated iodine being then titrated with standard thiosulphate.

A modification of the chromate titration consists of the precipitation of the lead as chromate by an excess of potassium dichromate, filtration of the precipitate, and titration of the excess of dichromate with a standard solution of ferrous sulphate.

Among other methods which have been proposed are :

- (i.) Precipitation with oxalic acid and ammonia, followed by a titration of the excess of oxalic acid with standard permanganate ;
- (ii.) Titration in neutral solution with $\frac{2}{5}N$ barium hydroxide to excess, the excess being titrated back with $\frac{N}{5}$ sulphuric acid ;
- (iii.) Titration with standard sodium sulphide until no further precipitate forms. Carbon tetrachloride is added to give a sharp separation of the lead sulphide ;²
- (iv.) Titration with potassium chromate, using *s*-diphenylcarbazine as indicator, a violet colouration being obtained with one part of chromate per million, if in a solution acidified with acetic or hydrochloric acid ;³ and
- (v.) Titration of a suitably prepared solution of lead acetate with potassium ferrocyanide, uranium acetate being employed as indicator.⁴

More difficulties exist in a convenient and reliable separation of the lead from the metals which accompany it than in its subsequent estimation. There is a constant divergence of opinion on these points, and none more than

¹ Cervi, *Chem. Cent.* (1904), ii. 1343.

² Koch, *Chem. Zeit.* (1908), 32, 124.

³ Oddo and Beretta, *Gazzetta* (1909), 39, i. 671.

⁴ Low, *Journ. Amer. Chem. Soc.*, October 1893.

on the question as to whether "metastannic acid" occludes lead when produced in the usual manner in nitric acid solution. Much work has been done and few conclusions reached. Under certain conditions it does seem almost impossible to extract all the lead. Merely opening out with nitric acid s.g. 1.20, diluting and filtering at once may be condemned from the start. Opening out with the minimum quantity of fuming nitric acid, evaporating just to dryness and then taking up in dilute nitric acid,¹ gives better results, whilst it has been found possible in many cases to extract the whole of the lead by dissolving in a small quantity of 1.20 acid, diluting with boiling water and digesting for at least half an hour.

Knöpfle² uses the fuming acid—1 c.c. for 0.1 gram alloy—and adds water drop by drop until no more red fumes appear, when the liquid is evaporated until the residue is just moist. Holzmann oxidises repeatedly with nitric acid 1.47, evaporates to dryness and takes up in 10 per cent. acid. Yockey³ dissolves in nitric acid 1.20, evaporates to dryness, heats for an hour at 120° C., moistens with acid, and extracts with water. Brearley and Ibbotson⁴ decompose with equal quantities of hot water and 1.43 acid, evaporate to low bulk, dilute with hot water, boil, and cool before filtering. V. Della Crose⁵ uses strong acid, but adds five grams of fine sand to half a gram of the alloy, evaporates to dryness, and extracts with water. The results of these various methods with three alloys are appended :

	1.	2.	3.
Westerkamp	62.74	83.31	84.12
Knöpfle	61.34	82.82	86.90
Holzmann	63.68	83.81	86.61
Yockey	61.32	80.98	81.30
Brearley and Ibbotson	62.40	83.70	84.32
v. Della Crose	59.46	80.70	85.50

¹ Westerkamp, *Arch. Pharm.* (1907), 245, 132.

² Knöpfle, *Zeit. Nahr. Genussm.* (1909), 17, 670.

³ Yockey, *Journ. Amer. Chem. Soc.* (1906), 28, 646.

⁴ Brearley and Ibbotson, *Analysis of Steel Works Materials*, Longmans.

⁵ v. Della Crose, *Ann. Chim. Anal.* (1909), 14, 245.

In each case the lead was determined as sulphate. The correct percentages, as given concordantly by three different methods, are 68.05, 83.52 and 89.04 respectively.

For alloys containing arsenic, antimony and tin it is often convenient to open out with hydrochloric acid and potassium chlorate, add tartaric acid, neutralise with caustic soda and precipitate the lead as sulphide with colourless sodium sulphide. (Copper may be retained in solution by the addition of potassium cyanide.) The precipitate may be dealt with as required, preferably worked up to the sulphate. The estimation as chloride previously mentioned provides a perfect separation from copper, antimony, tin, zinc, and iron, this being one of its most prominent virtues. The electrolytic method of precipitating as peroxide is useful as a separation from copper, zinc, iron, &c., but is interfered with by manganese, whilst it is only advisable to employ it in those cases where lead is a minor constituent.

Gravimetric Determination

The determination of lead as sulphide is rarely attempted, the precipitation of the metal in this form being usually followed by working up to sulphate; nor is the determination as chromate of sufficient value to claim more than mere mention. Lead is most conveniently determined gravimetrically as sulphate, chloride or molybdate. The determination as peroxide may also be found useful.

(A) *Determination as Sulphate.*—Lead sulphate is soluble in water to the extent of about 4 milligrams per 100 c.c. The gradual addition of sulphuric acid diminishes the solubility up to a certain point, when it begins to increase again. The most perfect precipitations are stated to be obtained from solutions of about normal degree of acidity; the authors' experience is that the amount of sulphuric acid can be increased up to 15 per cent. or more, without prejudicing the accuracy of the method. Alcohol also diminishes the solubility of lead sulphate in water, and this

reagent, added in large excess, is used by many operators instead of evaporating the solution to low bulk. The solubility of lead sulphate in hydrochloric and nitric acids is much greater than in sulphuric acid or in water, and these acids should therefore be completely eliminated from the solution. Moreover, the presence of certain alkaline salts in the solution increases the solubility of lead sulphate—ammonium acetate, *e.g.*, is frequently used as a solvent for lead sulphate, and sodium acetate, sodium thiosulphate, and alkaline chlorides in general, exert a more or less marked solvent action.

All these possible sources of error are eliminated by adding to the solution sulphuric acid (about 5 c.c. of which under ordinary conditions provide an ample excess), and boiling down as vigorously as possible until bumping usually makes it necessary to conduct the evaporation more slowly. The appearance of sulphur trioxide fumes denotes the complete removal of the more volatile acids and the conversion of any metallic chlorides (nitrates, &c.) into sulphates. After "fuming" for several minutes, the residue is allowed to cool somewhat, and water or dilute sulphuric acid added, so that the amount of free acid in the solution does not exceed about 20 per cent.

The separated lead sulphate is then collected on a previously prepared asbestos filter contained in a Gooch crucible, washed first with dilute sulphuric acid several times and then two or three times with alcohol to eliminate the acid. After drying, the crucible and contents are ignited at redness in the muffle or over a powerful burner. The ignition of precipitates which have been collected in this manner is very conveniently effected by placing the Gooch crucible inside an ordinary larger one from which it is separated by means of a ring cut out of a sheet of asbestos (Fig. 21).

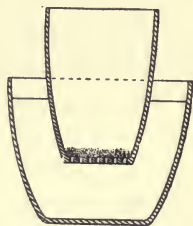


FIG. 21.

The residue after ignition is perfectly white and contains 68.31 per cent. of lead.

(B) *Determination as Chloride.*—Lead chloride is appreci-

ably soluble in cold water and freely in hot, but is quite insoluble in absolute alcohol. By evaporation of aqueous solutions containing lead and hydrochloric acid until the residue is only just moist, the addition of alcohol will therefore leave the whole of the lead in the form of lead chloride crystals. These are collected on asbestos in a weighed Gooch crucible, washed with alcohol, dried in the steam oven and weighed. They contain 74.51 per cent. of lead.

The applicability of the method is obviously restricted, the presence of all substances not soluble in alcohol being inadmissible. Fortunately the chlorides of the metals which occur with lead in white metal alloys are so soluble, and the conditions for a determination of lead are easily secured, so that the method is very useful and reliable. As applied to these alloys it is described on p. 192.

(C) *Determination as Molybdate*.—Lead is completely precipitated from neutral solutions or from solutions containing free acetic acid by means of a soluble molybdate. If the precipitation is made from pure solutions the colloidal white precipitate obtained cannot be manipulated satisfactorily; it can be filtered only with difficulty and very slowly, and when washed, almost invariably passes through the filter. If, however, relatively large amounts of alkaline salts, such as sodium or ammonium chloride, are present in the solution, the precipitate obtained is granular and dense, and can be filtered and washed with ease.

The solution containing the lead is therefore made slightly ammoniacal in order to neutralise any free mineral acids that may be present, and then just acid with acetic acid. Several grams of ammonium chloride are added, the liquid brought to boiling, an excess of ammonium molybdate added, the boiling continued for a minute, and the precipitate allowed to settle. Settling takes place almost at once, and the precipitate is then collected on "ashless" filter paper or preferably on ashless paper pulp, washed with hot water containing a few drops of ammonium acetate solution, ignited along with the filter at a red heat and weighed. PbMoO_4 contains 56.41 per cent. of lead.

Another form of the precipitation, and one which yields

a precipitate of a different physical condition, consists in the addition of the molybdate to a lead solution containing free hydrochloric acid. The ammonium molybdate solution should contain sufficient ammonium acetate to decompose the free hydrochloric acid or a sufficient quantity of the same reagent should be added subsequently. The lead molybdate so obtained is a very pale yellow precipitate with a beautiful silky lustre; it is capable of very rapid filtration and washing.

The relatively low lead contents of the molybdate, and the fact that it can be ignited along with filter paper without fear of reduction are distinct advantages. Moreover, copper, zinc and nickel yield no precipitate with ammonium molybdate under the same conditions, but it is not advisable to attempt the determination of lead by this method in the presence of tin or antimony.

A noteworthy disadvantage appertaining to the method lies in the fact that the weight of precipitate obtained is usually somewhat larger than is warranted by the amount of lead actually present. This is due to the precipitation of an acid molybdate, the excess of molybdic oxide present over that of the normal compound being roughly proportional to the excess of ammonium molybdate added. It is therefore always advisable to make a second precipitation. This is done by dissolving the ignited residue in a large excess of hydrochloric acid with two or three drops of nitric acid, adding hot water freely and then ammonium hydrate until a faint permanent turbidity is obtained. After clearing this with a drop or two of hydrochloric acid, a few drops of methyl orange solution are introduced, and finally ammonium acetate added until the yellow tint is obtained. Pure lead molybdate is thus obtained, and the excess of molybdic oxide present in the first precipitate thereby eliminated. The second precipitation can be easily accomplished in less than half an hour, (a fact which can be readily appreciated when it is borne in mind that the filtration and washing operations are very rapid), and the precipitate can be dried at the front of the muffle without fear of loss.

(D) *Determination as Peroxide*.—When an ammoniacal solution of lead is heated with ammonium or potassium persulphate, the metal is precipitated, more or less quickly according to circumstances, as the peroxide PbO_2 . It is essential that the solution should be ammoniacal, otherwise lead sulphate is co-precipitated. (Dittrich and Reise¹ determine lead in *acid* solution by precipitating with ammonium persulphate, weighing the metal finally as sulphate.)

The authors recommend that to a solution containing, say, 0.25 gram of lead, 50 c.c. of ammonium hydrate of s.g. 0.880 be added, and when the mixture has been brought to the boiling point, a hot aqueous solution of 5 grams of ammonium persulphate be added, and the boiling continued. In a very few minutes the lead is completely precipitated as the purple dioxide (hydrated), which immediately settles on standing and can be filtered at once. The precipitate is collected on asbestos in a Gooch crucible, washed with hot water containing a small quantity of ammonium nitrate, and finally once with water alone. (The precipitate passes through the filter if washed with water alone.) It is then dried rapidly at the corner of the hot plate, experiments having proved that the weight remains practically constant between 100° and 250° C.

The results obtained by this method are not so gratifying as those yielded by the others previously described, though the error is never very serious. The authors' experiments were not sufficiently conclusive to allow them to express a definite opinion on the cause of the discrepancies. Rupp² states that all his attempts to precipitate lead, bismuth, and manganese in the condition of their definite hydrated peroxides by the use of alkaline hydrogen peroxide, sodium hypochlorite, bromine dissolved in alkali or acetic acid, or alkaline potassium persulphate, gave precipitates of a lower and generally variable degree of oxidation.

¹ Dittrich and Reise, *Ber.*, 38, 1829.

² Rupp, *Zeit. anal. Chem.*, 42 (1903), 732.

Volumetric Determination

(A) *Molybdate Method*.—This method depends upon the quantitative precipitation of lead by standard solutions of ammonium molybdate, the end point being marked by the brown colouration given to a solution of tannin in water by a slight excess of ammonium molybdate. It may be performed upon either the ammonium acetate solution of previously precipitated lead sulphate, or upon the directly prepared nitric acid solution of lead. If the latter be employed all excess of nitric acid must be neutralised with ammonia, and then an excess of acetic acid added. The ammonium acetate solution merely requires the addition of a fairly large quantity of acetic acid. Bring the acid solution to the boil and then remove from the hot plate and titrate at once with a standard solution of ammonium molybdate, stirring vigorously the whole time. Before removing any of the solution for a spot test allow it to stand and settle for a few seconds. The end point is reached when the characteristic brown colour appears at once in the spot of tannin solution on the tile.

Sacher¹ has shown that some correction must be made for the volume of the liquid present during the titration. The following figures (which appear to be reliable) he supplies on the assumption that the strength of the ammonium molybdate solution is such that 1 c.c. is equal to 0.01 gram lead :

For 50 c.c. solution deduct 0.18 c.c. of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$

100	”	”	0.3	”	”
125	”	”	0.4	”	”
150	”	”	0.45	”	”
175	”	”	0.50	”	”
200	”	”	0.54	”	”
250	”	”	0.60	”	”
300	”	”	0.75	”	”

¹ Sacher, *Chem. Zeit.* (1909), 33, 1257.

The ammonium molybdate solution to which the figures refer contains 8.364 grams of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ crystals per litre.

The tannin solution should contain 1 part of tannin in 300 parts water.

(B) *Dichromate Method*.—This method depends upon the quantitative precipitation of lead chromate during titration with a standard solution of potassium dichromate. The end point is determined by observing the slightest excess of potassium dichromate by the purple colouration which it gives with silver nitrate—used outside the solution. For the success of the titration only weak acids must be present. Any strong acid must be neutralised with ammonia and then a quantity of acetic acid (B.P.) equal to about one-third the volume of the solution is added. The quantity of acetic acid is important, as if too great a quantity be employed no precipitation will take place. Fifty per cent. of acid is sufficient to prevent a perfect separation. About 30 per cent. is most suitable. The solution of the lead should be fairly concentrated and should be quite free from reducing metals.

When the acidity has been adjusted boil the solution, remove from the hot plate and quickly add from a burette the standard potassium dichromate. After each addition replace on the plate, and bring back to the boiling point. After boiling, allow to settle a little time before taking out any to test with the silver nitrate. The boiling of the solution during the titration is important but must not be overdone, as basic chromates may be formed and so ruin the estimation. Just before the end point is reached the precipitate falls very rapidly, this in itself acting as a fairly accurate and very useful indicator. If a sharp end point is to be obtained it is necessary to use a fairly concentrated solution of potassium dichromate. This means that each c.c. of the solution will be equal to a high percentage of lead, and consequently a large error will be very easily introduced.

The following figures were obtained in actual practice :

A	B	C
31.3 c.c.	84.5 per cent.	82.1 per cent.
31.4 „	84.9 „	82.6 „
31.7 „	—	81.9 „

A—are all three synthetic solutions, the theoretical figure for the $K_2Cr_2O_7$ required being 31.4 c.c.

B and C—are both bearing metals, the titrations being performed on solutions representing 0.5 gram of alloy.

Oddo and Beretta¹ have recommended the use of *s*-diphenylcarbazide as indicator. This is stated to give a violet colouration with one part of chromate in a million of the solution if it is acidified with acetic acid or hydrochloric acid.

A simple modification of the above consists of the addition of a known excess of potassium dichromate to the boiling acetic acid solution, the precipitate being allowed to settle. The whole is then filtered through asbestos and the excess of dichromate titrated with a standard solution of ferrous sulphate.

Electrolytic Estimation

As Peroxide.—Lead peroxide is readily formed as an anode deposit during the electrolysis of a nitric acid solution of lead. The only other metal which gives similar results is manganese, and in its absence lead may be estimated in the presence of most metals soluble in nitric acid. Usually copper is the only other metal likely to be present, and the estimation of these two, under certain circumstances, may be performed simultaneously. If, however, the lead is in considerable excess the estimation of the copper had better be done separately. It is stated² that the presence of sulphuric or chromic acids causes the results to be high, whilst arsenious and orthophosphoric acids produce low results.

¹ Oddo and Beretta, *Gazzetta* (1909), 39, i. 671.

² G. Vortmann, *Annalen* (1907), 351, 283–293.

The principal difficulty in connection with the estimation of lead as peroxide lies in the production of an adherent deposit. Unless the proper conditions are obtained the deposit scales off the anode and is usually lost. When only small quantities of lead are being dealt with (*i.e.* less than 0.1 gram) this difficulty is not a pressing one, but with quantities such as those obtained by the decomposition for analysis of a bearing metal it becomes serious. The best way to overcome the difficulty is to use a gauze electrode, a fairly high current density, and a strongly acid solution. For quantities of lead less than 0.1 gram an acid concentration of 10 per cent, is suitable, whilst for quantities up to 0.4 or 0.5 gram the concentration may be raised to 40 or 50 per cent., or even more. If a stationary electrode is employed, use C.D. of 1.0 to 1.7 and E.M.F. of 1.5 to 2.0 volts. With a revolving electrode (300 revolutions per minute) the E.M.F. may be raised to 3.0 to 4.0 volts and the C.D. to about 2.0 or 2.2. If it is desired to precipitate overnight, use C.D. 0.3 and E.M.F. 1.5 volt, when with a stationary electrode the decomposition is complete in about fifteen hours for 0.2 gram lead.

Naturally the time required depends upon the quantity of lead present as well as upon the current. With a rotating electrode up to 0.4 gram lead can be deposited in an hour with safety. The end point of the reaction is best determined by removing a drop of the liquid and testing it on a tile with sodium sulphide.

The deposited peroxide is carefully washed with a gentle stream of cold water, and then with absolute alcohol. It is then heated to about 200° C. for a few minutes. The deposit is usually impure, and Hollard and others recommend the factor 0.853 in place of the theoretical 0.866 for the lead content.

CHAPTER V

COPPER

THE determination of copper is easy once the metal has been obtained in a suitable solution. As copper is found in almost all commercial alloys, either as the result of design or as an impurity, the obtaining of such a solution is not always easy, and the methods of procuring it must always vary somewhat with the quantities present, and even more so according to the nature of the associated elements.

Although copper forms series of salts corresponding to two different states of oxidation, this fact cannot be taken advantage of to a great extent for volumetric purposes, since the cuprous salts in general are insoluble. The only way of making use of this characteristic is to reduce the copper and measure the quantity of reducing agent used, either by determining a difference or by some device such as is employed in the iodimetric determination. The insolubility of the cuprous salts and the relative ease with which all copper salts can be reduced to the metallic state can be utilised at any rate for purposes of separation, if not of determination.

Copper in both conditions forms additive compounds with ammonia, and with ammonium compounds, and their formation is valuable in the separation from many other metals. The sulphides also of both cuprous and cupric copper are insoluble in dilute hydrochloric and sulphuric acids, as well as in alkalies, although cupric sulphide is slightly soluble in sodium sulphide after digestion in warm solutions. They provide therefore a very valuable means of separation and also of determination.

Copper yields a so-called double cyanide with potassium which is perfectly soluble, providing a solution from which

sulphuretted hydrogen fails to yield a precipitate. All these principal reactions of the metal have been utilised for the determination of the metal.

There are comparatively few gravimetric methods which are suitable for use in technical laboratories. The convenient ones are usually slightly inaccurate, and those which are accurate are too tedious, being more suited to be exercises in pure analytical chemistry than workable methods of analysis. Amongst those that have been proposed and employed is the precipitation as sulphide followed by a careful ignition in a Rose crucible, through which a current of hydrogen is passed, which determines the composition of the residue as Cu_2S . This method is still recommended by authors of text-books on analytical chemistry as being the most accurate (as perhaps it may be), but its demerits are conspicuous and not few. Primarily there is the precipitation by hydrogen sulphide, in itself a long and unpleasant process. The filtration and washing of a sulphide is rarely a clean or neat operation, and this has to be followed by ignition in a stream of hydrogen, a proceeding which requires a special apparatus and considerable time and care. These disadvantages render the method quite unsuitable for technical purposes, and it has been almost entirely replaced by volumetric methods.

Another proposition is to precipitate the copper by means of sodium thiosulphate from an acid solution, whereby a mixture of sulphur and copper sulphide is obtained which furnishes at a red heat a residue of cupric oxide mixed with cuprous sulphide. As the percentage of copper is the same in both compounds, their relative amounts are of no consequence. This method is much better than the preceding one, but with large quantities of copper the amount of sodium thiosulphate required, results in a very large precipitate of sulphur, the coagulation of which by boiling, together with the subsequent filtration, occupies much time.

A rather more satisfactory method is the precipitation of the metal in the form of cuprous thiocyanate, with a subsequent ignition to oxide (or mixture of sulphide and oxide). The ignition may be avoided by filtering on a

Gooch crucible, and drying at 110° . Details of the method are given below.

Perkins¹ has proposed the precipitation of the copper as metal by means of aluminium foil, followed by a collection of the spongy precipitate on a Gooch crucible. The precipitation is made from solutions containing sulphuric acid.

An excellent method for the determination of copper when associated with tin, zinc, arsenic or antimony is that of Jannasch and Biedermann.² This is the precipitation as metal by means of hydrazine hydrochloride from a strongly alkaline solution. In the original of Jannasch and Biedermann the quantities of sodium hydrate recommended were not suited to the employment of the method upon such materials as those met with in ordinary work. By using a greatly increased quantity of alkali (forty parts instead of fifteen), and by running the copper solution, containing the minimum of free acid, drop by drop into the mixture of caustic soda and hydrazine hydrochloride, a perfect separation may be obtained. By redissolving the precipitated copper and determining it volumetrically the method is rendered still more convenient.

The electrolytic determination of copper is probably the simplest of its kind to be found anywhere in analytical laboratories. The element may be deposited successfully from very different sets of conditions, consequently the method can be applied to solutions obtained from very different sources. When a metal can be deposited from solutions containing either free acid, free ammonia, or various salts, there is little need for anxiety as to obtaining a suitable solution easily. As a result, the metallurgical chemist has a large number of methods at his disposal, and then by no means exhausts the list or its possibilities.

For his work in general, it may be assumed that a solution containing free acid will be the most suitable. Perkin recommends a solution containing 8 per cent. of free nitric acid, and uses then an E.M.F. of 2.0 to 2.8 volts with a

¹ Perkins, *Journ. Amer. Chem. Soc.* (1902), 24, 478.

² Jannasch and Biedermann, *Berichte* (1900), 33, 631.

current of 0.8 to 1.2 ampere, the solution being at a temperature of 50° C. With a solution containing 7 to 10 per cent. of sulphuric acid, to which is added a small quantity of hydroxylamine sulphate, he employs an E.M.F. of 2.5 to 3.2 volts with 0.8 ampere at 60° C. He also gives the necessary current details for an estimation in the solution of double cyanide of copper and potassium, obtained by just redissolving the precipitate obtained by adding potassium cyanide to a solution of the copper. Here the E.M.F. is 5.0 to 6.0 volts with 0.8 to 1.2 ampere. The last estimation requires two and a half hours; the first, one and a half to three hours.

Classen employs an ammonium oxalate solution (1.0 gram copper salt to 4 grams ammonium oxalate in 120 c.c. of water). Besides using an excess of ammonium oxalate, he adds a little oxalic acid to the solution. Electrolysing at 80° C. requires 0.5 to 1.0 ampere and an E.M.F. of 2.5 to 3.2 volts, the deposition being complete in two hours. For both nitric and sulphuric acid he prefers a more dilute solution than Perkin—using 5 per cent. of either—and electrolysing at 20°–30° C. with an E.M.F. of 2.2 to 2.5 volts and a current of 0.5 to 1.0 ampere. These conditions require five to six hours.

Neumann uses a current of 0.2 to 1.0 ampere with 1.5 volt for his nitric acid deposition, varying the percentage of nitric acid inversely as the current density. For sulphuric acid solutions he keeps the current density below 1.5 ampere, but uses an E.M.F. of 2.5 to 3.0 volts. He also recommends the ammonium oxalate method under the same conditions as Classen.

Rüdorff gives the details for an estimation in a solution containing 25 to 30 c.c. of ammonia with 4 or 5 grams of ammonium nitrate in a solution of 0.4 gram of copper as chloride, the volume of the liquid being 125 c.c. He completely precipitates the copper in three hours at 50° C., using 1.0 ampere and 3.3 to 3.6 volts. When adding only 20 c.c. ammonia and 2 to 3 grams of ammonium nitrate, he employs a current density of 2. Under similar circumstances Oettel employs currents as low as 0.07 to 0.27 ampere.

Rüdorff also employs the deposition from the double cyanide solutions, where he electrolyses at 50° C. with 1.0 ampere and 4.5 volts. With the double oxalate of copper and ammonium (containing an excess of three times of ammonia), he recommends 2.8 to 3.2 volts and 0.5 to 1.0 ampere at 60° C.

Smith uses a mixture containing 110 c.c. of water, 2.5 c.c. orthophosphoric acid, and 100 c.c. of saturated solution of Na_2HPO_4 . Electrolysis occupies 17 hours with an E.M.F. of 2.4 to 2.6 volts. For a solution containing sulphuric acid and a little hydroxylamine sulphate he uses a current density of 0.08 to 0.18 with E.M.F. 1.1 to 1.3 volt.

Luckow and Drowback use an ammoniacal solution of copper sulphate, and employ a current of 0.1 to 0.3 ampere with an E.M.F. of 2 volts rising to 3 volts. This takes from 6 to 7 hours, and gives very good deposits. Oettel and M'Coy use conditions otherwise similar, but add 4 grams of ammonium nitrate.

From these multifarious recommendations, the free-acid solutions with the conditions of Perkin or Classen, or the ammoniacal solutions of Rüdorff or of Luckow and Drowback, may be selected as most useful. As a rule these are the solutions most likely to be met with under the ordinary methods of opening out the alloys used.

The electrolytic process may be utilised for the separation of copper from many other metals by simply using the nitric acid solution. Under these conditions manganese and lead are obtained as peroxide deposits on the anode. Iron, cobalt, nickel, zinc, bismuth, &c., remain in solution. A nitric acid solution is not suitable in the presence of tin and antimony because of the precipitation of their oxides and the consequent occlusion of copper.

By far the most suitable methods for an ordinary laboratory are the volumetric methods. Many of these have been proposed, but none to beat the iodimetric method fully described below. Another very useful process is the titration of the copper in ammoniacal solution of potassium cyanide, the end point being marked by the replacement of the

azure blue colour by the characteristic lavender. For traces of copper the colorimetric estimation by comparison of tints produced in unknown and known copper solutions on the addition of potassium ferrocyanide is very suitable.

Parr¹ has proposed that the copper in solutions containing less than one per cent. of free nitric acid shall be precipitated as cuprous thiocyanate and this collected on asbestos. The filter and precipitate are then transferred bodily to a beaker, and heated to 70° C. with a few c.c. of caustic soda solution of 10 per cent. strength. Standard potassium permanganate is then added in amount sufficient to oxidise completely the cuprous oxide, the accomplishment of this being shown by the liquid assuming a permanent green tint. Excess of dilute sulphuric acid (one part to five of water) is then added, and when the liquid has become clear the titration is completed at 70° C. This is modified in a subsequent communication.² After returning the cuprous thiocyanate to the beaker, 10 c.c. of a 10 per cent. solution of caustic potash and 10 c.c. of ammonia of s.g. 0.96 are added, the titration being then conducted without delay until on warming to 45° C. to 55° C. the green colour remains. About a quarter of the amount of permanganate already used is added, and after cooling for five minutes, 25 c.c. of dilute sulphuric acid (one part to two of water) are added, and the titration carried to an end. Peters³ has proposed the precipitation of the copper as oxalate, filtering off, and estimation of the oxalic acid with potassium permanganate. Griggs⁴ titrates a copper solution with one containing 5.6 grams of potassium hydrate and 1.39 gram of hydroxylamine hydrochloride per litre, heating if required. The methods of Garrigues and Hawley are described below. The precipitation as cuprous thiocyanate has been utilised by Tsukakorki,⁵ who dissolves up the precipitate in nitric

¹ Parr, *Journ. Amer. Chem. Soc.* (1900), 22, 685.

² Parr, *Journ. Amer. Chem. Soc.* (1902), 24, 580.

³ Peters, *Amer. Journ. Sci.* (1900, iv.), 10, 359.

⁴ Griggs, *Chem. Centr.* (1904), ii. 367.

⁵ Tsukakorki, *Eng. and Min. Journ.* (1910), 90, 969.

acid and, after adding a slight excess of ammonia and removing this by boiling, adds 2 or 3 c.c. of acetic acid and then titrates with sodium thiosulphate.

Gravimetric Determination

(A) *Precipitation as Sulphide*.—The conditions governing the precipitation of copper by means of sulphuretted hydrogen have been well dealt with in Chapter III, and the general unsuitability of the process as a regular method of determining copper referred to in the foregoing summary. Certain points of interest in connection with the method nevertheless deserve mention. In the first place it is worthy of note that the precipitation can be made just as readily from sulphuric as from hydrochloric acid solutions, and if, *e.g.*, the amount of concentrated acid is about 5 c.c. per 100 c.c. of solution, and the latter is heated to boiling before passing the gas, the copper sulphide is generally completely precipitated when the solution attains room temperature. The precipitate thus obtained is dense, and settles quickly.

Copper sulphide must be washed with acidified hydrogen sulphide water, and the filter should be kept full all the time until washing is complete; all danger of oxidation and loss is thus removed. The subsequent drying and ignition in a Rose crucible in a current of hydrogen, whereby a residue conforming to the formula Cu_2S is finally obtained, are too well known to need description here. The fact, however, that copper sulphide precipitates, representing as much as 0.25 gram of copper, can be roasted quantitatively to cupric oxide makes it desirable to describe the *modus operandi*. Ignition in a muffle gives low results, calculating from CuO , and, whatever the cause may be, the results get less after each further ignition. Vervuert¹ therefore converts the sulphide to cupric oxide as follows:—The precipitate is detached as completely as possible from the paper and the latter burnt, the ash being ignited for a short time in a

¹ Vervuert, *Diss.*, München, 1908.

weighed porcelain crucible. After cooling, the main precipitate is introduced and very finely powdered. The crucible is then very gently heated, at first over a Bunsen flame to remove the excess of sulphur, and then the flame slowly increased, when the characteristic bluish flame will pervade the whole mass. The flame is then increased further until the bottom of the crucible is red hot, and after 10 minutes removed for a further 15 to 20 minutes to the blowpipe. No sulphate or sulphite is found in the final residue, which is entirely CuO .

(B) *Precipitation as Cuprous Thiocyanate*.—The solution employed must be perfectly free from nitric acid and nitrates. Neutralise all other strong acids with ammonia. Boil the solution and add an excess of sulphurous acid to reduce the copper, and then add ammonium thiocyanate (preferably not potassium thiocyanate) as a solution. Boil for a few moments, and then allow to stand. Filter on to pulp and carefully wash with hot water. Dry the precipitate and transfer to a crucible, gently igniting, to a mixture of cupric oxide and cuprous sulphide. Weigh as such (the copper percentage is the same in each compound). Results with this method are likely to be high. The method is not recommended.

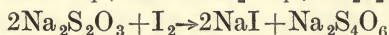
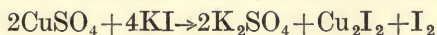
Van Name¹ has shown that the precipitation is quite a good one under certain conditions, and has demonstrated in particular that the acidity must be very carefully regulated according to the quantity of ammonium thiocyanate used in excess. Also if ammonium salts are present a considerable excess of ammonium thiocyanate must be employed. If much free acid is present, it had better be removed by neutralisation with ammonium bisulphite.

Volumetric Determination

(A) *Iodimetric*.—The reaction of cupric salts with potassium iodide producing cuprous iodide and iodine is extremely well known, and its application to quantitative

¹ Van Name, *Amer. Journ. Sci.*, 1900 (iv.), 10, 451, and 1902, 13, 20–26.

work is of very long standing. The estimation is one of the most exact; and, whilst it requires very strict adherence to the specified conditions, yet these conditions are fairly easy to obtain, and when obtained are easy to retain. Of all the various methods for the estimation of copper, this is probably the most satisfactory for all ordinary work:



The estimation must be performed in a solution containing no strong mineral acids. The quantity of copper is arranged to suit the standard solution of sodium thio-sulphate (or vice versa)—1 c.c. of which usually equals 0.0063 gram of copper, and the titration should be arranged to use not more than 40 c.c. of the standard solution. Obviously the solution must be free from either oxidising or reducing agents. Reducing agents will be oxidised at the expense of the precipitated iodine, and so will result in a low value for the copper. On the other hand, oxidising agents will liberate iodine from the potassium iodide, and so give a high result. These reactions are sufficiently keen to affect the estimation if the reagent is present only as a vapour. The titration should be performed in an atmosphere quite free from the ordinary fumes of the laboratory—acids, halogen, &c. Even such weak oxidisers as sulphuric acid will affect the potassium iodide. The action of acids, &c., in the solution has been thoroughly investigated recently,¹ and has shown that the following conditions must be observed:

(a) A fairly considerable excess of potassium iodide must be employed. Too small an excess of this reagent results in an incomplete precipitation of the iodine. In 50 c.c. of solution 0.2 gram excess is insufficient, but 0.6 gram is sufficient. For 0.2 gram copper in a solution of 50 c.c. bulk, 2 grams of potassium iodide are recommended and 5 grams if the volume is 100 c.c.

(b) The bulk must be kept low. With a large dilution the ordinary quantities of potassium iodide give results which are quite hopeless. If the volume is unavoidably

¹ Gooch and Heath, *Amer. Journ. Sci.* (1907), 24, 65–74.

high, the quantity of iodide must be increased in the proportions indicated above.

(c) The acidity must be regulated very carefully. The quantity that may be present varies with the acid. In a bulk of 50 c.c. up to 2 c.c. of concentrated sulphuric, hydrochloric or nitric acids have but little appreciable influence; 3 c.c., however, give an effect which can be estimated. With acetic acid 50 c.c. of 50 per cent. may be present in 100 c.c. of a solution without error, but with 5 grams of potassium iodide and 50 c.c. of concentrated acetic acid in 100 c.c. of solution free iodine is liberated. In all cases the quantity of iodine liberated varies inversely as the volume of the solution.

Kendall¹ has shown that when the iodimetric estimation has to be performed upon a nitric acid solution of a previously obtained precipitate of cupric oxide and cuprous sulphide, there is a danger of considerable error due to the presence of nitrous acid. He destroys this by the use of sodium hypochlorite solution of such a strength that 5 c.c. are equivalent to 30 c.c. of decinormal sodium thiosulphate. This solution is added till the copper solution turns a pale green. After allowing to stand for two minutes he adds 5 per cent. of phenol, and to avoid the production of nitrophenol, 20 per cent. sodium hydrate till a slight precipitate is produced. This he removes with acetic acid, and the solution is at once treated with potassium iodide and titrated.

Sujiura and Kobe² find the same difficulty, and also point out that nitrates constitute a danger by giving an unstable end point. On the other hand, solutions of cupric acetate give perfectly satisfactory results, the end point being quite sharp and quite stable. In order to obtain a solution containing nothing but acetates these workers dilute the solution of copper nitrate to 100 or 150 c.c., and after adding a little phenol phthalein, add a 33 per cent. solution of sodium hydrate till there is just a faint precipitation of copper, then N/5 sodium hydrate is added to a change of colour. Filter through ashless paper and wash with water. Transfer the

¹ Kendall, *Journ. Amer. Chem. Soc.* (1911), 33, 1947.

² Sujiura and Kobe, *Journ. Amer. Chem. Soc.* (1912), p. 818.

paper and precipitate to a flask and dissolve the copper hydroxide in 25 to 30 c.c. acetic acid. Then add potassium iodide and finish as usual. This method avoids all trouble due to the presence in the original solution of free mineral acids and also saves much concentration of the solution. Otherwise, neither this method nor that of Kendall present any real advantages over the usual method.

The essential conditions are probably obtained as accurately as is desired, by evaporating a solution of the copper in either sulphuric or nitric acid (preferably the latter) to a low bulk, cooling thoroughly and then neutralising with sodium carbonate. When a precipitate of blue copper carbonate is obtained take it up in a few drops of acetic acid. Boil the solution for a few moments, cool thoroughly and add potassium iodide in accordance with the requirements outlined above. Shake up thoroughly, allow to stand for two or three minutes and titrate at once with the standard solution of sodium thiosulphate, using a solution of starch to indicate the end point. The starch should not be added until the reaction has proceeded almost to completion, as shown by the almost total disappearance of the brown colour of free iodine in the solution. As in all titrations using starch as indicator, the liquid must be kept quite cold during the titration. (Pinniow¹ has shown the influence upon the starch reaction of other substances present in the solution. Eckstadt has stated that the blue colour is not developed in greater dilutions than 0.000025 N, and Meineke has shown that 100 c.c. of dilute starch solution required 0.13 c.c. N/100 iodine to produce the blue colour. The addition of more starch does not appreciably increase the sensitiveness, neither does the addition of non-electrolytes. The presence of electrolytes—best of all sodium sulphate—increases the sensitiveness tenfold. Here if the salt is present in quantities corresponding to a 0.22 N solution the blue colour is produced when the strength of the iodine solution exceeds $10^{-5} \times 0.17$ N.) Gerlinger² finds the end point to be obscure in the ordinary way, due to

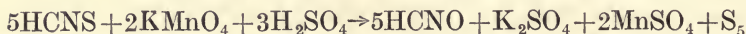
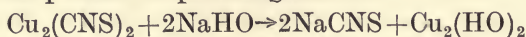
¹ Pinniow, *Z. anal. Chem.* (1902), 41, 485.

² Gerlinger, *Z. ang. Chem.* (1906), 19, 520.

the presence of the cuprous iodide, and to avoid this he adds sufficient potassium iodide to dissolve the precipitate. In order to avoid the same difficulty it is proposed by Peters to add excess of sodium thiosulphate and to bring this back again with a standard solution of iodine.

The equations given above show that one molecule of sodium thiosulphate is equivalent to one atom of copper. Hence 248 grs. of the crystallised salt ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) are equivalent to 63.3 grs. of copper, and so 1 c.c. N/10 sodium thiosulphate is equivalent to .0063 gr. copper. The sodium thiosulphate very rapidly deteriorates on standing and must be standardised frequently. The most suitable way of standardising is to use the solution directly against a standard copper solution—*e.g.* 6.3 grams per litre. The pure electrotype copper should be weighed off and dissolved in the minimum of nitric acid, the excess of this evaporated off and the paste of cupric nitrate dissolved in distilled water and made up to a standard volume. This gives the copper value of the solution at once.

(B) *Determination with Potassium Permanganate.*¹—This estimation may be used upon solutions containing large quantities of copper. The copper is precipitated as cuprous thiocyanate (as directed under the gravimetric processes), filtered off on to a pulp and thoroughly washed. The pulp should be packed very tightly and the greater quantity of the liquid passed through before the precipitate is thrown on to the filter. When thoroughly washed decompose the precipitate with a fairly strong solution of caustic soda, catching the washings in a clean flask. If the pulp has not been thoroughly well packed, the whole will lift on the addition of the sodium hydrate and the yellow cuprous hydrate will pass through. After washing the precipitate and filter, acidify the filtrate with a little dilute sulphuric acid and at once titrate the liberated thiocyanic acid with semi-normal potassium permanganate.



¹ F. G. Hawley, *Eng. and Min. Journ.* (1908), 86, 1155.

Garrigues¹ has modified this by transferring the precipitated cuprous thiocyanate to a beaker, adding a measured excess of standard sodium hydrate and then titrating this excess with standard acid.

(C) *Cyanometric Determination*.—The reactions of copper with potassium cyanide are well known, and not the least is the decolorisation of the ammoniacal solutions of the metal. The deep blue compounds, *e.g.* $\text{CuSO}_4 \cdot 4\text{NH}_3$, are completely changed by the addition of potassium cyanide in the presence of an excess of ammonium hydrate. The solutions must be free from all excess of acid, an evaporation to dryness being recommended, followed by extraction in water. Then for each 0.1 gram copper present add 10 c.c. ammonium hydrate and titrate with standard potassium cyanide solution, using the production of a pale lavender colour as the end point. The cyanide solution must be standardised against a known copper solution, such as that used for standardising the sodium thiosulphate in the iodimetric estimation.

Electrolytic Determination

In the general survey it has been shown that a very great choice is open to those wishing to employ this method of estimating, the metal being deposited from very diverse sets of conditions of solution contents, current densities, and voltages. For metallurgical work the most suitable solutions are those containing free nitric or free sulphuric acid. This determination of the copper is usually a preliminary to further estimations, most of the methods of analysis of the other constituents of the alloys being facilitated by this separation of the copper. Consequently the solution containing only these relatively volatile acids are eminently suitable for the subsequent operations. Also as most of the alloys are soluble in nitric acid and but few (relatively) are soluble in sul-

¹ Garrigues, *Journ. Amer. Chem. Soc.*, xix., No. 12, 1897.

phuric acid, the former acid will be most generally employed. For this acid two sets of conditions are available : (1) For an estimation lasting over several hours, *i.e.* using a stationary electrode, the conditions required are (i.) a solution containing not more than 10 per cent. of free acid, 8 per cent. being the most suitable ; (ii.) a current density 0.5 to 1.5, preferably about 1.0 ; and (iii.) the E.M.F. shall be 2.5 to 3.5 volts. Under these circumstances the copper is deposited completely in about three and a half hours (for 0.5 gram). If heated to 50° C., the deposition is complete in about an hour less. The percentage of nitric acid should not be increased beyond that mentioned or the deposit will be that of burned copper—*i.e.* will contain oxide. A similar result is obtained if the deposition is forced by raising the current density. (2) With a rotating electrode the percentage of free nitric acid may be increased to as much as 50 per cent., the current density to 2 and the E.M.F. to 5 volts. With these conditions and an electrolyte at 50° C., the precipitation is complete in about half an hour.

In either case the completion of the action may be tested for by taking out a few drops of the solution and adding to it a drop of potassium ferrocyanide, the absence of the reddish-brown precipitate indicating freedom from copper. When the deposition is complete, the deposit and the electrolyte must be separated before breaking the current. For the stationary electrode, the best way is to lower the anode till it almost touches the kathode and then to syphon off the liquid into another vessel. When the anode is nearly exposed, pour distilled water into the dish and continue to syphon. Continue the pouring and removing until the current drops to zero, then remove the anode and wash the kathode and deposit with alcohol, drying it quickly in the air. It is not advisable to heat the precipitate unduly. In the case of the rotating electrode, it should be lifted carefully from the solution, maintaining the current the whole time and allowing a stream of water from a wash bottle to flow down the electrode during the whole time. If these precautions are neglected in either case, the solvent action of the nitric acid on the deposit is so great that the results

obtained will be seriously low. A very few seconds are sufficient for the solution of several milligrams of copper. Stansbie¹ has shown that the solvent action is much more marked in the case of the stationary than the rotating electrode.

For a solution containing sulphuric acid the conditions required are : (i.) less than 10 per cent. free acid, (ii.) current density 0·8 to 1·0, (iii.) E.M.F. 2·5 to 3·2 volts, (iv.) temperature less than 65° C. With these conditions, less than four hours are required for the deposition of 0·5 gram on a stationary electrode.

The conditions for the other methods are indicated in the general survey, and more details may be obtained from the original papers.

¹ Stansbie, *Proc. Faraday Soc.*, 1912.

CHAPTER VI

BISMUTH

Gravimetric Determinations

THE estimation of bismuth is performed most satisfactorily by some gravimetric method, and several of these are known fairly well and can be worked with more or less ease. The most peculiar feature of the reactions of bismuth is the production of the well known insoluble white oxy compounds with the halogens and with other acid radicles. Of these only the halogen compounds are obtained in a state of purity sufficient to warrant their employment for quantitative purposes, the precipitation in the other cases being rather uncertain both as regards composition and completeness. The production of these compounds as a rule requires the absence of any considerable quantity of free acid, and whenever a solution containing a salt of bismuth is freed from acid, either by neutralisation or during the filtration of a precipitate and the consequent washing, there is a very great likelihood of the production of one of these basic compounds. This is a contingency to be guarded against in all operations with solutions containing bismuth, and may result in a serious loss of the metal if overlooked. The hydroxide of bismuth $\text{Bi}_2(\text{OH})_6$ is precipitated completely by alkalies, even so weak as ammonia, but the precipitation by means of the caustic alkalies is not suitable for quantitative work, as the alkalies exert a distinct solvent effect upon the precipitated hydroxide of bismuth. The carbonate of bismuth is precipitated by the ordinary alkaline carbonates, this compound being very useful for the accurate estimation of the metal. Another very useful precipitate is the phosphate, whilst bismuth resembles all the other metals of the group by having a sulphide perfectly insoluble in dilute

acids, which may be made use of for separations or estimations.

The actual compounds that are employed for gravimetric estimations are the oxide Bi_2O_3 , the oxychloride BiOCl , the sulphide, the phosphate BiPO_4 , and in addition the metal itself.

(A) *As Oxide*.—The oxide Bi_2O_3 is obtained usually by the ignition of the precipitated carbonate, if the bismuth happens to be in solution, but may be obtained from the nitrate or oxynitrate as well as from the carbonate, if any of these compounds are obtained in the solid state. The oxyhalides are not suitable for this ignition, and if these are mixed with mercuric oxide to convert them to the oxide there is a considerable loss by volatilisation.¹ If bismuth oxychloride be present it is best to dissolve it in the maximum quantity of hydrochloric acid, to add mercuric oxide to this, to evaporate to dryness, and then extract with a very little water. The precipitates are mixed with more mercuric oxide and ignited very gently until the mercuric chloride is seen to be coming off, then heated more strongly until the ignition is quite complete.² Frequently the bismuth oxide may show black specks, and if these are ever seen the precipitate should be treated with fuming (or concentrated) nitric acid and ignited afresh to ensure the proper precipitate being weighed. During any of these ignitions the precipitate must be kept away from contact with any actual flames, otherwise there is likely to be a reduction (in part) to the metal. Most usually the oxide is obtained by precipitating the bismuth with a soluble carbonate. The metal is best in a nitric acid solution (in fact this may be taken as a general rule unless a statement to the contrary is made), and to this a concentrated solution of ammonium carbonate should be added in excess. The precipitate is washed with hot water and may be ignited in a platinum crucible to bismuth oxide Bi_2O_3 . Heintz³ states that the precipitate is the basic carbonate $(\text{BiO})_2\text{CO}_3$, or a still more complex one contain-

¹ Volhard, *Zeit. für anal. Chem.*, 20 (1881), 288.

² Smith and Heyl, *Zeit. f. anorg. Chem.*, 7 (1894), 82.

³ Heintz, *Zeit. f. anorg. Chem.*, 4 (1893), 76.

ing this compound. The actual composition is immaterial if only nitrates are present in the solution, as the precipitate ignites quantitatively to the oxide. If there are chlorides present the Cl' ions must be removed by evaporation with concentrated nitric acid, as if they are allowed to remain they will appear in the precipitate and produce a partially volatile compound of bismuth. If the alkalies, sodium or potassium carbonates be employed in place of the ammonium carbonate, the resulting precipitate is likely to be contaminated with sodium or potassium salts. The oxide may be obtained quite satisfactorily from the hydroxide. As stated above, the strong alkalies (sodium and potassium hydroxides) are not suited for the production of this precipitate because of this solvent action upon the bismuth hydroxide. Even ammonia must be used with some care to prevent any similar action, and only a slight excess of the reagent should be allowed in the solution. Löwe preferred to wash these precipitates with a dilute solution of ammonium nitrate. The oxide Bi_2O_3 which is produced, is somewhat volatile at temperatures below its melting point, and in consequence any undue overheating is to be avoided.

(B) *As Sulphide*.—For those solutions which contain SO_4'' or Cl' ions, and which in consequence are not suited for the foregoing process (as they would give basic precipitates of chloride or sulphate), Treadwell uses the sulphide precipitation. This compound has all the vices inherent to metallic sulphides and no corresponding virtues. None of the workers, except Treadwell, who have tried this method like the precipitate sufficiently to allow them to use it for the final weighing as such. Rose redissolved it and converted it to the carbonate, and thence to the oxide, and his example has been followed fairly widely. The precipitation is performed in all cases in acid solutions by means of a rapid stream of sulphuretted hydrogen. The precipitate Bi_2S_3 is collected on a Gooch crucible and washed with water saturated with hydrogen sulphide. Then the water is removed by absolute alcohol, and the sulphur which contaminates the precipitate is taken out by freshly distilled

carbon bisulphide. Löwe, not using a Gooch crucible, dried his precipitate and then treated it with a concentrated solution of sodium sulphite to take out the sulphur, filtering out the purer precipitate. Most workers prefer to dissolve up the precipitate and convert it to either oxide, phosphate or oxychloride. It is not possible to ignite the sulphide mixed with sulphur in a stream of hydrogen (as is done for the sulphides of copper or nickel), as there is always a certain amount of reduction to the metal. Neither is it possible to roast the precipitate to oxide Bi_2O_3 , as the resulting compound always contains some sulphate.

(C) *As Metal*.—Bismuth is precipitated as metal quite easily in the wet way by several reagents, although in the dry its reduction is not at all easy. Hydrogen will only reduce the oxide of bismuth partially, and that at temperatures at which the oxide itself is distinctly volatile. For the precipitation of the metal from solution there have been several good proposals. Obviously those metals with a greater solution pressure will precipitate the bismuth, and zinc, cadmium, tin, iron and lead have been employed. Of these the last is the one chosen, the lead being introduced as a flat strip into an acid solution. This process is not used very much, as other more convenient methods have been put forward, and also because it is difficult to prevent some oxidation taking place. Frequently the oxides or oxychloride precipitations of bismuth are impure or of doubtful composition, and one very convenient method of precipitation is to fuse with potassium cyanide in a porcelain crucible. By this fusion the metal is liberated as a number of small bright globules, which may be united into one globule by careful handling :



This requires about five times the weight of the bismuth compound of potassium cyanide. When cold the melt is extracted with water and the bead filtered off, as all the resulting salts are soluble in water. The metal is dried with alcohol and weighed. Frequently it is contaminated by

material from the crucible. After weighing, the bead should be dissolved in nitric acid, the solution diluted and the impurities which are sure to be insoluble filtered off. The weight of the impurity is then subtracted from that of the original bead.

Vanino and Treubert¹ use a wet reducing agent—formaldehyde in alkaline solutions. The solution contains the bismuth with as little free acid as possible, and to this is added the formaldehyde in sufficient excess, then a considerable excess of a 10 per cent. solution of sodium hydroxide. The whole is then warmed until the supernatant liquor is quite clear, when the precipitate is washed by decantation with a dilute solution of formaldehyde several times. Finally the precipitate is pressed together with a glass rod and transferred to a Gooch crucible. It is washed with absolute alcohol and dried at 100° C. This precipitate is likely to give high results because of the sodium or potassium hydroxide that is always left behind to contaminate the metal. To overcome this the metal may be dissolved in dilute nitric acid and precipitated as carbonate, weighing up as oxide. Sometimes the precipitation of the bismuth is not quite complete—probably owing to the formation of some oxide which is dissolved by the alkali that is present. As a rule this method gives accurate results.

Muthmann and Mawrow² use hypophosphorous acid for the reduction. They prepare a fairly concentrated bismuth solution, not too freely acid, and to this they add an excess of hypophosphorous acid. This solution is digested just below the boiling point until the supernatant liquor is quite clear and until the addition of a further small quantity of the boiling acid produces no colouration in this liquor. The precipitate is collected on a Gooch crucible and washed with hot water and then alcohol.

Brunck³ uses sodium hyposulphite ($\text{Na}_2\text{S}_2\text{O}_4$) as reducing agent and obtains a precipitate of metal, which is not pure, containing a little sulphide and a little oxide. It

¹ Vanino and Treubert, *Ber.*, 31 (1898), 1303.

² Muthmann and Mawrow, *Zeit. f. anorg. Chem.*, 13 (1897), 209.

³ Brunck, *Ann. Chem.*, 336 (1904), 290.

may be treated by roasting to oxide, or by redissolving and precipitating as the carbonate or as the phosphate.

(D) *As Oxychloride*.—A method that has become almost standard is the precipitation as bismuth oxychloride, BiOCl . This may be done from solutions of the metal as nitrate if some Cl' ions are supplied. The most usual method is to prepare an almost exactly neutral solution by means of dilute ammonia (stopping when any precipitate is formed) and then to add just enough hydrochloric acid to make the solution faintly acid. The resulting solution is digested for an hour, the bismuth oxychloride filtered off and weighed as such after drying at 100°C . The Cl' ions may be supplied by means of sodium or potassium chloride with equally good results, though the production of the accurately neutral solution is not so easy under the circumstances. Another method of procedure is to prepare a solution containing the bismuth with a *very little* free hydrochloric acid, then to pour this solution into a large bulk of water, and to allow the precipitate to settle. When the precipitate has settled more water should be added to test for any further turbidity, and if none is produced the precipitate is treated as before. If either SO_4'' , or $\text{PO}_4'''^1$ or AsO_4''' ions are present the precipitate of bismuth oxychloride is almost certain to be contaminated with the basic precipitates of these radicles with bismuth. To avoid the error likely to arise from this source, it is usually recommended that the resulting precipitate be estimated by the production of a bead of the metal obtained by fusing with potassium cyanide followed by purification from silica and similar impurities.

(E) *As Phosphate*.—Many workers have found the precipitation as bismuth phosphate a very satisfactory method of estimation. This compound is a fine white crystalline body quite insoluble in dilute nitric acid in the presence of PO_4''' ions. The orthophosphate is quite stable, and is in fact the only one, the others—meta- and pyrophosphate—passing into it. Various conditions have been proposed,

¹ This is not correct, as H_3PO_4 dissociates under ordinary conditions into $\text{H}_2\text{PO}_4'$ and HPO_4'' , but no misconception is likely to arise by the use of PO_4''' , though they are not likely to exist.

though all workers appear to prefer to keep the solution moderately acid throughout the precipitation. Stähler and Scharfenberg¹ add a 10 per cent. boiling solution of the sodium hydrogen phosphate to a very dilute solution of bismuth nitrate, and if the solution becomes alkaline they restore its acidity by the addition of a few drops of nitric acid. After boiling thoroughly for a few minutes the precipitate is allowed to settle, and then filtered on to a Gooch crucible, the washing being done with 1 per cent. nitric acid and then a solution of ammonium nitrate (though probably better results are obtained if this latter is omitted).

Moser uses an $\frac{N}{5}$ solution of diammonium hydrogen phosphate, which he adds to the solution containing the minimum of nitric acid required to keep up the bismuth. The phosphate solution is added in slight excess only, and the solution is then boiled until the heavy bismuth orthophosphate settles to the bottom. The washing of the precipitate is done with hot water. Probably this is the quickest and easiest of all the methods for the gravimetric estimation of bismuth.

Volumetric Determinations

With one exception the volumetric estimation of bismuth is not performed by the direct titration of the bismuth solution with another reagent, the methods, as a rule, depending upon the addition of an excess of some precipitant, the removal of the precipitate, and the estimation of the excess of the precipitant in an aliquot portion of the filtrate, by a direct titration. The exception to the rule is the method (one of the oldest) of Pattison Muir,² and depends upon the precipitation of bismuth with either potassium chromate or dichromate, using the chocolate-coloured precipitate with silver nitrate as the indicator for the end point. Two or three variations of this have been proposed. In the first one the potassium chromate in

¹ Stähler and Scharfenberg, *Ber.*, 38 (1905), 3862.

² Pattison Muir, *Journ. of Chem. Soc.*, 24 (1877), 465.

excess is added to the bismuth solution, and the precipitate of bismuth chromate filtered off. The excess of chromate in an aliquot portion of the filtrate is determined by means of the titration with sodium thiosulphate solution, of the iodine liberated from potassium iodide added to the liquid. This requires that the bismuth chromate precipitate shall not hydrolyse during the filtering and washing (if any washing is done), and to prevent this as far as possible, Rupp and Schaumann¹ use a fairly concentrated solution of potassium chromate and make the precipitation in the cold, the bismuth solution containing a little free acid. Another method takes the precipitate of bismuth chromate and estimates the CrO_4 in this by adding excess of ferrous sulphate, and then titrating the excess of ferrous iron by potassium permanganate.

Another similar method depends upon the precipitation of the bismuth as phosphate. To a solution of the metal as nitrate in dilute nitric acid an excess of sodium acetate is added, and then a known excess of disodium hydrogen phosphate solution. The precipitate is filtered off and the PO_4''' ions in an aliquot portion of the filtrate estimated by means of uranyl acetate. The end point of this titration is obtained by the use of either tincture of cochineal or of potassium ferrocyanide, used externally. Muir has also tried to make this a direct titration, but owing to the difficulty of the production of a sharp end point the method is difficult.

The oxalate of bismuth has been used for a volumetric method. First the simple oxalate of bismuth was precipitated, and then partially hydrolysed by boiling with water. This gave a basic oxalate of bismuth of constant composition in which the oxalic acid was titrated with potassium permanganate after liberation with sulphuric acid. This method has been abandoned largely in favour of the precipitation of a double oxalate of bismuth and potassium by a solution of potassium oxalate. The method is to add a known quantity of standard potassium oxalate solution and then to filter off the double oxalate (which Reis² states

¹ Rupp and Schaumann, *Zeit. f. anorg. Chem.*, 32 (1902), 362.

² Reis, *Berichte*, xiv. 1172.

to be $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot \text{K}_2\text{C}_2\text{O}_4$), and to estimate the excess of potassium oxalate in an aliquot portion of the filtrate. It is not advisable to add any great excess of potassium oxalate in this method, and the solution should not contain any large excess of free acid—even acetic. The precipitation with potassium oxalate is quite complete and of the known composition, but not so with either sodium or ammonium oxalate.

Other volumetric methods that have been suggested include the precipitation of the bismuth with an excess of potassium iodate, followed by the removal of the precipitate and the estimation of the excess of potassium iodate in the filtrate by the addition of potassium iodide, and the titration of the liberated iodine with sodium thiosulphate. This is stated to be unreliable by Rupp and Krauss,¹ as the precipitate is not pure bismuthiodate $\text{Bi}(\text{IO}_3)_3$, but $\text{Bi}(\text{OH})(\text{IO}_3)_2$.

Another method is to precipitate the bismuth as sulphide, and then to add this precipitate to a known solution of standard silver nitrate. Filter off the silver sulphide and determine the excess of silver in the filtrate by titration with ammonium thiocyanate, using ferric alum as indicator. Yet another method precipitates bismuth with ammonium molybdate, thus obtaining a precipitate of $\text{Bi}(\text{NH}_4)(\text{MoO}_4)_2$. This is dissolved in sulphuric acid and the molybdenum in the solution determined by reduction in a Jones' Reductor followed by titration with potassium permanganate. The volumetric methods that are employed most frequently are those of the oxalate or the phosphate precipitations followed by the determination of the excess of precipitant in the filtrate.

Electrolytic Determinations

Bismuth is one of the very worst of all metals to estimate electrolytically. In general this is due to three factors. First, bismuth is very close to hydrogen in the electrochemical list; secondly, bismuth has a very great tendency

¹ Rupp and Krauss, *Archiv. d. Pharm.*, 241 (1903), 435.

to the formation of anodic deposits of various compounds of bismuth and oxygen; thirdly, it is a very difficult matter to make the deposited bismuth stick to the kathode, it being found more frequently lying loose or floating about. Each of these difficulties requires a special treatment if any satisfactory result is to be obtained. In practice it is found that the electrolytic deposition of bismuth is not worth the trouble. The first method is designed to overcome the likelihood of the discharge of hydrogen in preference to the deposition of bismuth. This is performed in an apparatus of the form described on p. 15 (*q.v.*), which is designed particularly with a view to the maintenance of a constant kathode potential, this being measured continually by the inclusion of a standard mercury electrode and a capillary electrometer. By carefully arranging, the potential is kept as near as possible to the discharge voltage of the bismuth ions and as far as possible from that of the hydrogen. It is stated that under these circumstances a very satisfactory deposition of the bismuth may be obtained. Sand uses a gradually decreasing current, finishing up at about 0.2 ampere, whilst he arranges that the voltmeter shall register 0.63 volt at first and shall not be allowed to rise during the operation to more than 0.9 volt. His solution has 0.2 to 0.3 gram of bismuth, with 2.5 c.c. concentrated nitric acid, and 8 grams of sodium tartrate in 100 c.c. of water. This he stirs by a rotating anode at 900 to 1000 revolutions per minute. The deposition requires from ten to fifteen minutes, and the end point is detected by the use of ammonium sulphide.

The other method which is designed to overcome the second and third difficulties mentioned above is the one which employs a mercury kathode. This method has been suggested for various metallic and non-metallic ions, but no one is estimated more satisfactorily by these means than is bismuth. It is certainly an effective way of getting over the difficulty of obtaining deposits which will adhere to the electrode and not oxidise. E. F. Smith¹ has described a

¹ E. F. Smith, *Journ. Amer. Chem. Soc.*, 27, 1255.

very convenient beaker in which to make the depositions. He fuses a platinum wire through the bottom of a tall beaker and bends it round on both sides so that there will be an accurate contact between the platinum and a copper disc placed below the beaker on the outside, and with a layer of clear mercury in the bottom of the beaker on the inside. The whole apparatus is washed quite thoroughly with water, with alcohol, and then with ether, and allowed to dry in a desiccator. When quite free from ether it is weighed. The same operations are performed after the deposition has taken place. (Another form of mercury kathode is that of Cain, described on p. 13.) This apparatus is used with some success. Another method is to deposit the amalgam itself by the electrolysis of a mixed electrolyte containing bismuth and mercury. It is essential that the proportion of mercury to bismuth should be at least four to one, or otherwise the amalgam will be coated by a black deposit of oxygen compounds of bismuth. Most usually a solution of the two nitrates is employed containing about 0.5 gram of bismuth to 2.0 grams of mercury. The electrolysis is conducted with currents up to 1.0 ampere and an E.M.F. of 3.5 volts. The deposited amalgam may be washed and dried quite thoroughly in the ordinary manner. Vortmann has employed a mixture containing hydrochloric acid, his solution being 0.2 to 0.8 gram of bismuth oxide, 1.0 to 3.0 grams of mercuric chloride, and enough hydrochloric acid to dissolve the bismuth oxide, the acid being diluted with 50 c.c. of 96 per cent. alcohol. Despite this, the deposition will be made most usually from nitric acid solution rather than the hydrochloric, because (1) the chlorine that is liberated is not very good for the electrodes, (2) nitric acid solutions of bismuth are obtained much more frequently than hydrochloric acid solutions.

For the deposition in the ordinary way upon flat platinum electrodes in the usual circuit the following solutions have been suggested. Smith and Knerr¹ and Thomas and Smith² use a solution containing 0.15 gram of bismuth as sulphate,

¹ Smith and Knerr, *Journ. Amer. Chem. Soc.*, 8, 206.

² Thomas and Smith, *Journ. Amer. Chem. Soc.*, 5, 114.

with 3 c.c. of sulphuric acid and 150 c.c. of solution. This is stated to require very great care if an adherent deposit is to be obtained and washed. Wieland¹ and Smith and Saltar² employ an ordinary nitric acid solution containing just sufficient free acid to prevent the separation of any basic salts. Brunck³ uses a solution containing less than 2 per cent. of nitric acid and about one-tenth per cent. of bismuth. The current density is 0.1 to 0.5 and the E.M.F. is never allowed to exceed 2.0 volts. The current density is arranged to vary inversely as the quantity of bismuth that is present. Other solutions that have been proposed are (1) those containing the bismuth as a double oxalate with either ammonia or potassium; (2) a solution containing free ammonia and sodium hypophosphite; (3) a solution in which the bismuth is associated with either citric or tartaric acids, the solution being either freely alkaline or freely acid; (4) the bismuth associated with acetic acid and some borax. Another suggestion to obtain a complete precipitation, and also to prevent the almost inevitable shaling and oxidation during drying, is to deposit cadmium along with the last parts of the bismuth and also as a layer over the bismuth deposit. A known quantity of cadmium as sulphate is added a little time before the end of the deposition and weighed up along with the bismuth. Despite all the work that has been expended in the efforts to produce a satisfactory deposition of bismuth for practical purposes, it is doubtful whether the estimation is ever likely to be made upon the small quantities that are present in commercial alloys.

¹ Wieland, *Berichte*, 17, 1612.

² Smith and Saltar, *Zeit. anorg. Chem.*, 3, 416.

³ Brunck, *Berichte*, 35, 1871.

CHAPTER VII

ANTIMONY

THERE are three oxides of antimony, Sb_4O_6 , Sb_2O_4 , and Sb_2O_5 , the first and last of which give rise to the antimonious and antimonic salts respectively. The trioxide is white at ordinary temperatures, turns slightly yellow when heated, and fuses at a dark red heat to a yellow liquid. At higher temperatures it sublimes unchanged in the absence of air, but gives the tetroxide in its presence. The latter oxide, formerly regarded as a compound of the tri- with the pentoxide, is a white powder which remains solid and stable at temperatures up to 900°C . It results from the ignition, with access of air, of either of the other two.

The halogen compounds of trivalent antimony are solid, the pentavalent compounds, of which the chloride and fluoride only are known with certainty, being liquid under ordinary circumstances. The latter are energetically decomposed by water with production of hydrogen chloride and antimonic acid. Hydrochloric acid solutions of trivalent antimony when taken to dryness and then heated further on the water bath only, lose weight in the form of volatile trichloride; in the presence of free hydrochloric acid the solutions can, nevertheless, be heated to 110° without loss.

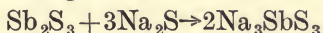
There are two sulphides which have already been referred to in Chapter III. The trisulphide Sb_2S_3 exists in two forms, an unstable amorphous red modification which at 200° to 220° in absence of air changes to the stable grey modification. This change can also be effected in solution by heating at 200° with water,¹ also at the ordinary temperature on long standing in acid solution. The pentasulphide cannot

¹ Schurmann. *Ann. Chem.*, 249, 336.

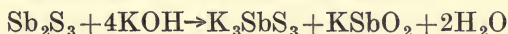
be obtained in a pure condition by precipitation with hydrogen sulphide; it results from the acidification of alkaline antimonates, such as Schlippe's salt, $\text{Na}_3\text{SbS}_4 + 9\text{H}_2\text{O}$.

The orange-red precipitates, obtained from -ic as well as from -ous solutions by hydrogen sulphide, are of gelatinous consistency, and it is therefore very difficult to free them by washing from salts adsorbed from solution. It has also been shown by Schieder,¹ Beckett,² and other observers, that the black crystalline precipitates are never pure, and chlorine in particular is obstinately retained by them even after heating to 300° . Red antimony trisulphide precipitates, after washing and drying at 100° , contain about 1 per cent. of chlorine, and the black crystalline precipitates about 0.3 per cent. From hot antimonious solutions, red precipitates only are yielded at acid strengths up to 1.5 normal hydrochloric acid, but at 1.75 normal strength the black crystalline modification is obtained. Thus a difference in acid content of only 0.9 gram per 100 c.c. of solution suffices to produce a difference in the consistency, colour and density of precipitated antimony trisulphide. According to Beckett pure antimony trisulphide can be obtained from hydrogen sulphide precipitations, only by heating the washed and dried precipitate in a stream of hydrogen sulphide to a temperature of 400° ; precipitates from solutions of pentavalent antimony yield the same product by this treatment, viz. the dark grey crystalline modification of antimony trisulphide.

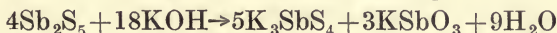
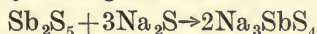
Antimony trisulphide is freely soluble in excess of alkaline sulphides yielding thioantimonites.



In strong alkalies it also dissolves with the formation of a mixture of antimonite with thioantimonite.



Similarly the pentasulphide yields thioantimonates and metantimonates by analogous reactions.



¹ Schieder, *Diss.*, München, 1908.

² Beckett, *Diss.*, Zurich (1909); *Chem. News*, 102, 101.

Acidification of these solutions results in a re-precipitation of antimony sulphide, which however is not complete, even from sulphide solutions.

Metallic antimony and the antimony of white metal alloys is not soluble in hydrochloric and other non-oxidising acids in the absence of air, but comparatively feeble oxidants such as ferric salts promote solution, and reagents like aqua regia, potassium chlorate and hydrochloric acid, and bromine with hydrochloric acid dissolve antimony freely. The metal is not attacked by dilute sulphuric acid; concentrated acid yields sulphur dioxide and a solution of antimonyl sulphate.

Antimony is precipitated as metal from its solutions by tin, lead, cadmium, zinc, nickel, cobalt, iron and copper, but not by bismuth and mercury. Under certain circumstances the metal is also precipitated from its solutions by stannous chloride, hypophosphorous acid, and sodium hydrosulphite.¹ Iodides, ferrous salts and sulphur dioxide reduce acid solutions of pentavalent antimony to the tri-valent condition, but salts of hydrazine and hydroxylamine are without effect. The converse change can be effected by means of chlorine, bromine, hydrogen peroxide, bromates, permanganates, &c.

Hydroxyl compounds yield precipitates with antimonious solutions which consist at first of basic salts such as the oxychloride SbOCl ; an excess of the hydroxyl compound yields the hydrated oxide $\text{Sb}_4\text{O}_6 \cdot \text{H}_2\text{O}$ (antimonious acid), whilst a still larger excess of potash, for instance, redissolves the precipitate, forming a soluble antimonite KSbO_2 . Solutions of pentavalent antimony give a similar series of products, viz. oxychloride SbOCl_3 , antimonie acid H_3SbO_4 , metantimonate KSbO_3 , and antimonate K_3SbO_4 .

Gravimetric Determination

Antimony is determined gravimetrically as trisulphide, tetroxide, and sometimes as metantimonate of sodium. The

¹ Staddon, *Chem. News*, 106, 199.

determination as sulphide is effected, according to Neher, by heating at 240°C . to 260°C . in a current of carbon dioxide. Henz, who characterises the method as the best of all for the determination of antimony, recommends 300°C . as the upper limit of temperature. All forms of antimony sulphide are converted by this treatment into the dark grey stable modification. Vortmann and Metzl arrange the conditions of precipitation so as to secure the dark crystalline precipitate in the wet condition; it is finally dried at 110°C . and weighed. The Rose and Finkener method of converting the sulphide into metal by heating in a stream of hydrogen gas is not generally practised at the present time.

The determination as tetroxide (Bunsen) by heating the previously precipitated sulphide with fuming nitric acid is susceptible of great accuracy when care is taken to prevent mechanical loss during the operation. The determination as sodium metantimonate is too tedious for general purposes, and owes its approximate accuracy to compensating errors.

(A) *Determination as Sulphide.* (a) *Method of Henz.*¹—Hydrogen sulphide is passed into the solution containing either tri- or pentavalent antimony, in the cold for about 20 minutes. The solution is then heated slowly without interrupting the passage of the gas, and the current continued for another 15 minutes longer at or near the boiling point of the solution. After settling, the precipitate is collected on an asbestos filter in a Gooch crucible, previously weighed after heating to 280° to 300°C . Washing, which is conducted by decantation at first, is done with water acidulated with acetic acid, through which sulphuretted hydrogen has been passed, until the washings show no chlorine reaction. This is usually the case when they show a slight turbidity. The precipitate is dried first of all at a temperature not exceeding 130° , and is finally heated in a current of carbon dioxide up to 300°C . The special tubes and drying ovens recommended for this last operation may be dispensed

¹ Henz, *Zeit. für anorg. Chem.*, 37, 1 et seq.

with for ordinary purposes. Antimony trisulphide contains 71.42 per cent. of antimony.

(b) *Method of Vortmann and Metzl*.¹—The acidity of the antimony solution is first adjusted so that in every 100 c.c. there are 24 c.c. of concentrated hydrochloric acid. The solution is then heated to boiling, and a rapid stream of sulphuretted hydrogen delivered. The precipitate is yellow at first, then it turns to a red which rapidly darkens in shade until it finally becomes black. At the same time the precipitate becomes denser and more crystalline. These changes are hastened by frequent shaking during the half hour, which usually suffices for almost complete precipitation. An equal volume of water is then added so as to rinse the sides of the precipitation flask; this causes a yellow turbidity which is attributed to the precipitation of a small amount of antimony sulphide not previously precipitated. The solution is again heated and the gas passed for a few minutes longer, when the liquid will have become clear again. After cooling, the precipitated trisulphide is collected in a weighed Gooch crucible on asbestos, washed first with water and afterwards with hot alcohol. It is dried at 105° to 110°, and weighed.

(B) *Determination as Tetroxide* (Bunsen).²—This method consists in the conversion of the trisulphide into tetroxide by means of nitric acid, and the following procedure will be found to give good results.

The black sulphide, obtained by precipitation, according to Vortmann and Metzl's method, or any suitable variation of it, is collected on filter paper and washed with a solution of ammonium nitrate of about decinormal strength until the washings give no chlorine reaction. (This wash liquid is better than water, because the latter at times gives turbid washings before the precipitate is chlorine-free.) The precipitate is then dried, separated from the filter paper as completely as possible, and put on a watch-glass. The filter paper is torn into small pieces and treated at least six times with small quantities of yellow ammonium sulphide, the

¹ Vortmann and Metzl, *Zeit. f. anal. Chem.*, 44, 526.

² Bunsen, *Ann. Chem. u. Pharm.*, 106, 3.

extractions being passed through a very small filter and collected in a large porcelain crucible. After taking to dryness the main precipitate is added, the crucible covered with a watch-glass, and a small quantity of nitric acid s.g. 1.42 added. Gentle heat is applied, if necessary, until the residue is white. After cooling, the separated sulphur is oxidised by adding two or three c.c. of fuming nitric acid s.g. 1.55, the watch-glass being quickly replaced to prevent loss due to the somewhat violent action which sets in. After taking to dryness on a water bath, and then expelling the sulphuric acid by heating cautiously over a small naked flame, the crucible is placed finally in the muffle, where it may be safely left, provided the temperature does not reach 950°C . Antimony tetroxide contains 78.98 per cent. of antimony.

Volumetric Determination

The volumetric methods for the determination of antimony are the most satisfactory of all, and consist in the reduction of the metal from the pentavalent to the trivalent condition followed by a titration. This is done either by titrating directly back to the pentavalent state or by adding an excess of some reagent which does this, and at the same time liberates some other substance capable of ready estimation. Fortunately, antimonious salts are not as excessively difficult to maintain in that condition as are the stannous salts, and consequently their accurate determination is somewhat simplified. Moreover, there are several methods available in which the antimonious salts may be produced and determined, in the presence of tin as well as of many other metals.

(A) *Titration of Antimonious Salts with Potassium Bromate*.—The antimony from the “opening-out” of an alloy or the solution of a precipitate of antimony sulphide is usually in the antimonious condition, and the solution frequently contains free halogen, which has been employed in some form to effect or assist solution. The latter must be entirely removed by boiling, and the acidity of the solution

adjusted to about 50 per cent. of concentrated hydrochloric acid. The solution is heated to boiling, and sufficient sodium sulphite added to reduce the antimony. A large excess of this reagent should be avoided, as the sulphur dioxide generated is not removed very readily from these solutions until their bulk is considerably reduced, and then the excess results in much unpleasant "bumping." It has been observed also that after boiling down in this way, and then diluting either with water or diluted hydrochloric acid, a further evolution of sulphur dioxide is obtained. A most satisfactory way of removing the gas is to boil over a naked flame (supporting the flask by a Langmuir strap), a filter plate having been placed in the flask before the heating. The authors find that about 3 grams of sodium sulphite provide not too large an excess in the reduction of one decigram of antimony, though individual practice may discover that complete reduction is obtained with considerably less than this amount.

When the sulphur dioxide has been expelled, 50 per cent. hydrochloric acid is added up to a suitable volume, the solution is brought to a boil, and a standard solution of potassium bromate run in at once after adding a few drops of a solution of methyl-orange. The end point is marked by a bleaching of the indicator.

If any previous knowledge of the approximate amount of antimony present is available, it may usefully be employed in calculating the probable quantity of bromate required, so that the indicator can be added when the titration is nearing completion. The end point is thus more sharply defined, and experience of this useful method shows that the difference between the readings of the burette may amount to as much as 0.3 c.c. of decinormal potassium bromate according to whether the indicator was added at first or towards the end of the titration.

In the absence of any knowledge concerning the amount of antimony present, it is better to retain a very small portion of the solution which is being titrated in a separate vessel, add the indicator to the main portion, and titrate rapidly to a discharge of the colour, then introduce the

retained portion together with more indicator, and finally determine the end point drop by drop.

The reaction may be formulated thus:



according to which 167.01 grams of potassium bromate are equivalent to 360.6 grams of antimony. A convenient solution holds 2.7852 grams of the bromate crystals per litre, and each c.c. represents 0.006 gram of antimony. The solution, which remains constant in strength after long standing, is standardised with pure metallic antimony or tartar emetic.

(B) *Determination by Means of Iodine Monochloride.*—This method is particularly convenient, as it may be carried out in the presence of almost any metal likely to be met with in the ordinary alloys. The iodine monochloride employed is not the pure substance, but may be prepared quite easily by dissolving 10 grams of potassium iodide and 6.44 grams of potassium iodate in 75 c.c. of distilled water and 75 c.c. of concentrated hydrochloric acid. When the dark brown precipitate, which is at once produced, has completely dissolved, one globule of chloroform is added to the solution, and the colour of this globule adjusted to that of very dilute iodine by the addition of a few drops of a dilute solution of either potassium iodide or iodate as required. When made in this way the solution keeps very well. (See Appendix.)

The original recommendations for this method, suggested working in sulphuric acid solution, to which a little concentrated hydrochloric acid had been added. It is preferable, however, to work in solutions of chlorides quite free from sulphates.

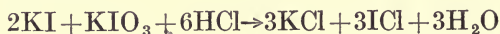
Assuming the existence of a solution containing the whole of the antimony in the pentavalent condition, the reduction to the antimonious state may be effected either by sodium sulphite directly in the acid solution or by neutralising with ammonia or caustic soda and then reducing with sulphurous acid. The latter process is preferable, because it not only allows the solution to be cleared quickly of the

excess of the reagent, but by virtue of the neutralisation of the free acid prior to the reduction produces a solution of known acidity, and thus it is quite easy to adjust the final acidity. As the degree of acidity of the solution is important—50 per cent.—this latter advantage is considerable.

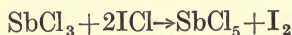
When all the sulphur dioxide has been removed from the solution, the acidity is brought to the required degree by adding just less than an equal volume of hydrochloric acid, and the mixture cooled thoroughly under the water tap. The latter operation is performed as quickly as possible to minimise the risk of oxidation of the antimonious chloride.

The cold solution is then transferred to a flask provided with a stopper and a narrow neck—a graduated flask answers the purpose admirably—and 5 c.c. of chloroform, 15 c.c. concentrated hydrochloric acid and 5 c.c. of the iodine monochloride solution added in the order named. The mixture is shaken very thoroughly, allowed to stand for five minutes, and the liberated iodine titrated with a standard solution of potassium iodate. The end point is marked by complete decolorisation of the chloroform. This point is observed most readily by inverting the flask and so obtaining the chloroform as the base of a narrow column in the neck of the flask.

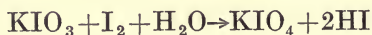
The iodine monochloride solution is the result of the following reaction :



The result of the addition of the reagent to antimonious solutions may be formulated thus :



and the titration of the liberated iodine proceeds according to the equation

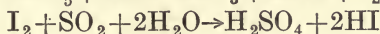


A convenient strength of potassium iodate solution is 3.5670 grams per litre. Of this solution each c.c. is equivalent to 0.004 gram of antimony.

(C) *Titration with Iodine Solution.*—The titration with iodine is one of the oldest and most reliable volumetric

methods for the determination of antimony, and can be employed under a fairly wide set of conditions.

The antimony is reduced, if necessary, from the pentavalent to the trivalent condition, and frequently by means of sulphur dioxide, in the presence of a small quantity of potassium iodide acting as a catalytic agent.



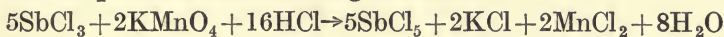
The reduction may be carried out in a slightly acid solution. After the expulsion of the excess of sulphur dioxide, a little tartaric acid is added and the solution cooled. Starch solution is then introduced, and one or two drops of iodine solution in order to generate the blue colour. This is then discharged by the addition of ammonia or sodium hydrate, the slight excess of alkali thus obtained being then just removed by the addition of a few drops of acid. An excess of about 20 c.c. of a saturated solution of sodium bicarbonate solution is then added, and the solution titrated with standard iodine.



from which 1 c.c. of decinormal iodine is equivalent to 0.006 gram of antimony.

As a variation, an excess of iodine may be used, and this determined by means of a standard solution of sodium thiosulphate.

(D) *Titration with Potassium Permanganate.*—Cold solutions of antimonious chloride can be titrated in the presence of free hydrochloric acid by means of potassium permanganate, the usual permanent pink colour being taken as the end point of the following reaction:



The adjustment of the acidity of the solution is important, an acid concentration of 1 volume hydrochloric acid in 5 volumes of the solution being found most suitable. With less acid than this low results are obtained, and in solutions containing more acid, chlorine is generated, leading to high results. If the antimony is present originally in the pentavalent form, it should not be reduced with an alkaline sul-

phite. The presence of the alkali metals produces yellow solutions which make the end point difficult of observation.

The method is frequently applied to precipitates of antimony sulphide obtained in the ordinary course of analysis. Petriccioli and Reuter¹ dissolve the sulphide in concentrated hydrochloric acid, and expel the sulphuretted hydrogen formed by heating short of boiling. The presence of the gas is at once detected by the appearance of a red turbidity or precipitate on adding cold water. When the sulphuretted hydrogen has been completely expelled, the solution is diluted until a slight milkiness is obtained, which is then just cleared with diluted acid before cooling and titrating.

Electrolytic Determination

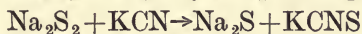
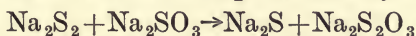
Antimony can be electrolytically deposited from several kinds of solutions. It can be obtained from solutions containing free sulphuric or hydrochloric acid, and from oxalate solutions, but the metal is generally determined electrolytically by the decomposition of a thioantimonite solution obtained by dissolving antimony trisulphide in sodium sulphide.

When chloride solutions are electrolysed, provision must be made for dealing with the chlorine generated. Mechanical arrangements such as the use of a diaphragm or the introduction of a brisk current of air are used, but it is simpler to make use of a salt of hydrazine. This is added at the beginning of the electrolysis, and from time to time during its progress when the yellow colour of the solution shows it to be necessary. The acidity of the solution should be about 20 per cent. Other conditions are : a current of 0.8 ampere falling gradually during the electrolysis to half this amount, a voltage of 1.3 rising to 1.7, and cold solutions. Rotation of the kathode is also desirable. The deposits are frequently non-adherent.

¹ Petriccioli and Reuter, *Zeit. f. angew. Chem.*, 14, 1179, and *Zeit. f. anal. Chem.*, 43, 116.

The electrolysis of sulphuric acid solutions was investigated by Sand,¹ with the object of obviating the positive error of the Classen method referred to in the next paragraph. The solution should contain about 50 per cent. of sulphuric acid, also two or three grams of common salt or, better still, monochloroacetic acid, together with a small quantity of hydrazine sulphate added a few minutes after the beginning of the electrolysis. A current of 1 to 1.5 ampere is used at first, with a difference of potential of about one volt, whilst the solution is heated to 100° C. or 110° C. and the kathode rotated. The deposition is not quite complete, though the maximum error does not exceed 0.4 per cent. of the total antimony present, and it is frequently as low as 0.1 per cent.

The electrolysis of thioantimonite and thioantimonate solutions, originally proposed by Parodi and Mascagni,² was exhaustively investigated by Classen³ and later by Henz,⁴ Förster and Wolf,⁵ Dormaar,⁶ Sand,⁷ and Hallmann.⁸ Complete deposition cannot be effected from solutions containing polysulphides, and it is more difficult to deposit from thioantimonate solutions than from thioantimonites, hence the introduction into the electrolyte of such substances as sodium sulphite and, better still, potassium cyanide.



When the surface of the kathode is etched or roughened, the antimony is deposited on it as a silver-grey closely-adherent film, but the results obtained are invariably in excess of the actual amount of metal present. The excess varies between 1.5 and 2 per cent. according to most authorities, but it is not uncommon to obtain somewhat larger

¹ Sand, *Trans. Chem. Soc.* (1908).

² Parodi and Mascagni, *Zeit. f. anal. Chem.*, 18, 588.

³ Classen, *Berichte*, 14, 1622; 17, 2462; 18, 1104; 27, 2060.

⁴ Henz, *Zeit. f. anorg. Chem.*, 37, 36.

⁵ Förster and Wolf, *Zeit. f. Elektrochem.*, 13, 205.

⁶ Dormaar, *Zeit. f. anorg. Chem.*, 53, 349.

⁷ Sand, *Zeit. f. Elektrochem.*, 13, 326.

⁸ Hallmann, *Dissert.*, Aachen (1911).

figures. This positive error is usually attributed to the formation of some oxide, though it has been stated by Scheen¹ to be due to mother liquor mechanically enclosed, and he therefore advocates the use of a polished kathode. As the same set of conditions generally yields the same plus error, a correction factor can be employed and satisfactory results thus obtained. The method provides an easy separation of antimony not only from lead, copper, &c., but also from arsenic and tin, when the proper conditions are secured and adhered to. As, moreover, these conditions are precisely those which occur in the ordinary course of analysis, it is not surprising that the Classen method is the one generally employed for the electrolytic determination of antimony. The following are the most suitable conditions: the antimony sulphide precipitate is dissolved from the filter with about 80 c.c. of sodium sulphide solution of spec. grav. 1.4, and the liquid diluted up to 140 to 150 c.c. Two or three grams of potassium cyanide are added, the temperature raised to 60° C. to 70° C., and the solution electrolysed with a current of 1 to 1.5 ampere at 2 to 3 volts. Two decigrams of antimony are deposited under the above conditions in the same number of hours. The results, as already stated, require correction by a factor to be determined empirically by the operator.

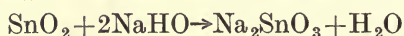
¹ Scheen, *Zeit. f. Elektrochem.*, 14, 257.

CHAPTER VIII

TIN

TIN forms two series of salts, stannous and stannic, corresponding to the oxides SnO and SnO_2 respectively. The former, a greyish-black powder, is of no analytical importance; the latter, a white, difficultly fusible solid, results from the oxidation of the metal or its sulphides, and from the dehydration of the so-called stannic and metastannic acids. The latter are the products of the hydrolysis of stannic salts, and also of the opening-out of tin alloys with nitric acid. The white, slimy precipitates thus obtained contain varying amounts of water according to circumstances, and the existence of a hydrate of definite composition is questionable; these substances must be regarded as hydrogels of stannic oxide. They readily adsorb phosphoric acid and other substances from solution; it is, for example, well known that the residue obtained by opening-out a bronze with nitric acid always holds copper, also lead and iron if present in the alloy, whilst practically all the phosphorus of a phosphor-bronze is to be found in the insoluble residue. The common method of determining tin in bronzes by collecting the residue insoluble in nitric acid must therefore take account of the associated impurities. This is done usually by fusing the ignited and weighed residue with not less than six times its weight of sodium thiosulphate, or with a mixture of equal parts of sodium carbonate and flowers of sulphur. On leaching out with water, sulphides of copper, lead, and iron are left and the tin passes into solution as a yellow sodium thiostannate, Na_2SnS_3 . It is seldom that one fusion suffices to take all the stannic oxide into solution; the authors found, *e.g.*, that one gram of a bronze of 10 per cent. tin contents yielded a

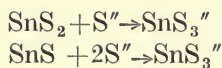
residue of unchanged stannic oxide, which was comparatively large even after two fusions, and they have entirely discarded the process. Fusion of stannic oxide with sodium hydrate or carbonate produces sodium stannate, soluble in water and also in dilute alcohol, differing in the latter respect from the corresponding antimony compound.



Stannic oxide is easily reduced to metal by fusion at a red heat with potassium cyanide.

The halogen compounds of tin are for the most part soluble in water, but the solutions are particularly prone to hydrolysis, and soon become turbid on standing. Stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, melting at 38°C ., dissolves to a clear solution in water if air is excluded, but if air obtains access the addition of hydrochloric acid is necessary to prevent the separation of an oxychloride, and also, on account of the powerful reducing properties of the solution, of a piece of metallic tin to prevent oxidation. Stannic chloride, SnCl_4 , is a liquid at ordinary temperatures which fumes strongly in air, boils at 114°C ., and is energetically decomposed by water, a large excess of which completely hydrolyses it. The volatility of stannic chloride is sometimes taken advantage of in analytical chemistry; there is, however, no danger of loss of tin by boiling dilute solutions, and the temperature of strongly acid ones can be raised with safety to 120°C .

Of the two sulphides of tin, only the yellow SnS_2 is of importance analytically; the conditions determining its precipitation have already been discussed. It dissolves with ease in alkaline sulphides, forming thiostannates. Stannous sulphide does not yield thiostannites by an analogous reaction, and it is not soluble unless the alkaline sulphide contains polysulphides, in which case thiostannates are formed.



The determination of tin in its alloys is mostly done by a volumetric method. The principal one is a titration of a stannous solution containing free hydrochloric acid by

means of a standard solution of iodine or ferric chloride. As the weak oxidising power of these substances renders them inactive in strongly acid solution towards trivalent antimony and arsenic, the determination of tin can be made in the presence of these metals. Knecht¹ titrates stannous solutions with a standard solution of titanium trichloride, air being excluded, but the method has not found much favour in general practice. Palmer² operates in alkaline solution on stannous solutions with potassium ferricyanide, and determines the tin indirectly by a back titration of the ferrocyanide formed, with permanganate. The titration of stannic solutions by means of potassium ferrocyanide was proposed by Gräger³ in 1865 and much later by Luckow.⁴ The former operates on stannic chloride solutions and delivers the standard ferrocyanide solution until a precipitate ceases to form, and the latter uses oxalate solutions containing also free sulphuric acid.

Tin is determined gravimetrically either by precipitation from its solutions as a hydrated stannic oxide or as stannic sulphide, with subsequent ignition to stannic oxide in either case. Precipitation from stannic solutions with ammonia or from stannous solutions with hydrogen peroxide and ammonia, yields a hydrogel of stannic oxide containing all the tin present in the solution, but the use of this process is obviously very much restricted by the fact that so many other metals yield precipitates with ammonia. Of wider application is the precipitation, by hydrolysis, of highly diluted acid solutions, a separation of tin from all the other metallic constituents of the commoner alloys, except antimony, being thus provided. Both forms of precipitation labour under the disadvantages created by the adsorptive properties of the precipitate. The separation of tin as stannic sulphide by means of sulphuretted hydrogen followed by ignition to oxide is, on the whole, much more serviceable, and is dealt with fully below.

¹ Knecht, *Berichte*, 37, 3318.

² Palmer, *Zeit. f. anorg. Chem.*, 67, 317.

³ Gräger, *Journ. f. prakt. Chem.*, 96, 330.

⁴ Luckow, *Chem. Zeit.*, 15 (1891), 1491.

The electrolytic determination of tin is possible from alkaline or from acid solutions, as well as from solutions containing alkaline sulphides and also oxalic acid. Thus Engels¹ employs a chloride solution containing about half a gram of hydroxylamine hydrochloride, together with some tartaric acid and ammonium acetate, and Quintaine² electrolyses sulphuric acid solutions in the presence of ammonium salts, whilst Lampèu³ uses alkaline stannate solutions. None of these methods have met with as much success as the depositions from alkaline sulphide or oxalic acid solutions, of which particulars are given below.

Gravimetric Determination

(A) *Precipitation as Hydrated Stannic Oxide.* (a) *By Means of Ammonium Hydrate.*—If the solution contains the tin in its quadrivalent form, an excess of ammonia only is added; this is supplemented by hydrogen peroxide in the case of bivalent tin solutions. The liquid is digested for some time to allow the precipitate to collect together, the precipitate filtered, washed with water containing ammonium nitrate, dried and ignited, along with the filter, to stannic oxide which contains 78.81 per cent. of tin.

In addition to the metals which are precipitated by ammonia, oxalates, tartrates, &c., must be absent from the original solution. Alkaline stannate solutions must first be acidified with hydrochloric acid before adding ammonia, otherwise they yield no precipitate at all.

(b) *By Hydrolysis of Stannic Solutions.*—All stannic solutions, if free from the halogen acids, are hydrolysed completely by diluting and allowing them to stand long enough in the cold, whilst if warmed the tin separates completely in a few minutes. The usual procedure is to dilute the solution so that the amount of hot water added is at least ten times that of the nitric (or sulphuric) acid present.

¹ Engels, *Berichte*, 28, 3187.

² Quintaine, *D. R. P. Nr.*, 118358.

³ Lampèu, *Journ. Soc. Chem. Ind.*, 30, 128.

The liquid is then digested for some time to ensure more rapid filtration. Precipitation is favoured by the presence of certain substances such as sulphuric acid, ammonium sulphate and ammonium nitrate, but salts of potassium and sodium are adsorbed from the solution by the metastannic acid, and are not therefore admissible. The opening-out of tin alloys with nitric acid followed by dilution of the solution is the most commonly occurring example of this method, the disadvantages of which have already been mentioned.

Should the original solution contain free hydrochloric acid it will be found that Treadwell's directions lead to good results. According to these the solution is treated cautiously with ammonia until it just turns methyl-orange yellow, a few drops of nitric acid added, the solution largely diluted, from 10 to 20 grams of ammonium nitrate added, and the mixture digested at the boiling point for about a quarter of an hour. After a short time for settling the precipitate is filtered as hot as possible, and washed with hot water containing nitric acid and ammonium nitrate. If the filtration is slow it is advisable not to commence washing at all, but to return the precipitate by means of a stream of water from the wash bottle to the precipitation beaker, and digest for some time longer with water acidified with nitric acid.

(B) *Precipitation as Sulphide from Hydrochloric Acid Solutions.*—The tin must be in the quadrivalent condition, and the solution must be free from nitric acid or other oxidising agents. The acidity should be adjusted approximately to normality, *i.e.* the solution should contain about 3.6 per cent. of hydrochloric acid. A rapid stream of hydrogen sulphide is passed through the solution, which is slowly heated to about 60° C., kept at that temperature for a few minutes, then raised to about 90° C., kept there for a few minutes longer, and finally lowered to 60° C. again, the gas being passed in all the time. The precipitate obtained in this way settles and filters well. Without waiting, however, for complete settling, it is filtered hot through an ashless paper and washed with a hot solution of ammonium nitrate until the washings no longer react with silver nitrate. The

precipitate is then dried, detached as completely as possible from the filter paper and placed temporarily in a watch-glass. The paper is then burnt and ashed in a porcelain crucible, the ash moistened with nitric acid and the residue gently ignited. The main precipitate is then added and finely ground up with the rounded end of a glass rod. The lid is replaced and a gentle heat applied by means of a small Bunsen flame, after which the lid is removed (there being no further danger of loss by decrepitation), the crucible placed in an inclined position, and a stronger heat applied. Roasting begins and spreads gradually with a bluish flame and development of sulphur dioxide through the whole mass. The crucible is rotated from time to time, so as to expose a fresh surface to the air for oxidation. The last portions are best oxidised by moistening with nitric acid. The final heating, to expel traces of sulphuric acid, must be conducted over the blowpipe or at the highest available temperature of the muffle. After cooling, a small piece of ammonium carbonate is added, the temperature gradually raised to that of full redness, maintained there for two minutes, the crucible again cooled and weighed. The treatment with ammonium carbonate is repeated, if necessary, until a constant weight is reached.

Volumetric Determination

(A) *Titration with Iodine*.—A solution of stannous chloride constitutes a powerful reducing agent, and it readily reacts with all the usual oxidising agents employed in volumetric analysis. Of these, comparatively weak oxidants like iodine and ferric chloride are without effect in strongly acid solution on trivalent antimony and arsenic, and they are therefore particularly well suited to the determination of tin in ordinary white metal alloys. The actual acidity of the solution should not be less than binormal at the time of titration with iodine, and it may nearly reach 50 per cent. by volume of the solution without acting prejudicially. The reduction to the stannous condition can be brought about by a number of metals, *e.g.* zinc, cadmium, iron, aluminium,

and finely divided nickel, lead, or antimony. The authors prefer antimony which has been thoroughly ground in an agate mortar to a very fine powder free from all glistening particles. In all titrations of acidified stannous solutions, the oxidising effect of the atmosphere must not be overlooked. The following procedure, based upon the foregoing remarks, will be found to give excellent results.

The solution, containing the tin either in the -ous or the -ic or both conditions, is treated with hydrochloric acid in amount sufficient to constitute about one-third of the total volume, which should be between 300 and 400 c.c. After adding about one gram of the powdered antimony, the liquid is brought to the boiling point and then boiled vigorously so as to project the finely divided antimony from the bottom of the flask well up into the liquid. Two minutes' boiling suffices for the reduction, under these conditions of acidity, of a decigram of tin in the form of stannic chloride. Without removing the antimony, the flask and contents are then cooled off under the water tap as rapidly as possible, whilst a brisk current of carbon dioxide is passed through the solution. When cold a small piece of white marble is introduced and the liquid is titrated as quickly as possible with iodine solution and a starch indicator. From the reaction



it follows that 1 c.c. of $\frac{N}{10}$ iodine solution is equivalent to 5.95 milligrams of tin.

(B) *Titration with Ferric Chloride.*—This method is based on the reaction $\text{SnCl}_2 + 2\text{FeCl}_3 \rightarrow \text{SnCl}_4 + 2\text{FeCl}_2$, according to which the tin to be estimated must be present as stannous chloride. The solution to be titrated must be strongly acid, and must be titrated hot and very quickly with a comparatively strong solution of ferric chloride. If not more than one minute is occupied in the titration, there is no necessity for displacing the air from the titration flask by carbon dioxide. The titration should not be performed in artificial light, but the end point is not difficult to deter-

mine in daylight, being marked by a yellow tinge, which an excess of one drop of the ferric chloride solution imparts to hot, colourless, and strongly acid solutions, at not too great a dilution. In this case the volume should be about 150 to 200 c.c. Salts of iron, nickel, cobalt, aluminium, zinc, cadmium, antimony, lead, arsenic and copper are without influence, but precipitated metallic antimony, copper and arsenic are attacked by hot acid solutions of ferric chloride. The method is limited to the determination of relatively large amounts of tin, on account of the strength of the ferric chloride which it is necessary to employ to enable the substance to constitute the indicator.

The standard solution usually employed contains about 90 grams of the ordinary hydrated solid in a litre, and is made by dissolving first of all in 100 c.c. of hydrochloric acid, taking to dryness to remove traces of nitric acid, taking up again in 150 c.c. of acid and diluting to a litre. Each c.c. of such a solution is approximately equivalent to 0.02 gram of tin. It is standardised by dissolving one gram of Kahlbaum tin, contained in a small flask provided with a bung and Bunsen valve, in a large excess of strong hydrochloric acid. The liquid is heated to boiling and maintained in constant but gentle ebullition until the metal is completely dissolved, when the titration is at once made.

A modification of the above method consists in adding an excess of ferric chloride solution, the exact excess being determined by means of a standard solution of stannous chloride, using molybdic acid as the indicator.

Electrolytic Estimation of Tin

Only two methods appear to have been evolved and employed generally for the electrolytic estimation of tin. The first of these uses those compounds of tin—the thiostannates—formed by the action of ammonium sulphide upon the sulphides of tin which are insoluble in acids. Unlike the deposition of antimony, the sodium sulphides may not be employed, and the ammonium sulphide should be made to

contain a certain proportion of polysulphides by the addition of flowers of sulphur. If the precipitated tin sulphide be dissolved in this, the solution may be electrolysed by a current density from 1.0 to 1.8 and an E.M.F. from 4.0 to 4.5 volts, according to several workers. The authors have found this a distinctly unpleasant method to work. The reagent is not nice to handle, the deposits as a rule are dirty and contaminated with sulphur and the deposition takes a long time. Frequently, too, the deposition is incomplete unless carried on for very protracted periods. They have found that a method based upon that of Classen and v. Reis,¹ who employ the double oxalate of tin and ammonium, is much to be preferred. Classen and v. Reis found that although this solution gave good metallic deposits, yet it also allowed the precipitation of stannic oxide in the liquid, and that to keep up this precipitate it was necessary to add some free oxalic acid. (The precipitation is due to the oxidation of the ammonium oxalate to ammonium carbonate with the consequent formation of an alkaline solution.) They use 4 grams of ammonium oxalate to 0.50 gram of stannic chloride, in a solution neutralised with ammonia, and then made just acid by the addition of some 2 or 3 grams of oxalic acid. With this solution they employ a current density of 0.3 to 0.4 with an E.M.F. 2.8 to 3.5 volts. In another scheme they add 10 c.c. of acetic acid and electrolyse at normal temperatures with 0.50 ampere per square decimeter. The authors prefer to use a solution containing ammonium oxalate and free hydrochloric acid. They find that a solution containing 0.25 gram of tin as sulphate or chloride, mixed with 5 to 8 grams of ammonium oxalate and with 10 c.c. of hydrochloric acid (*i.e.* about 3 to 5 per cent. of the solution) allows of a very satisfactory analysis. The best results are obtained with a low current density (down to 0.2) and an E.M.F. of 3.5 volts. It is not advisable to increase the current density too much.

One of the more recent proposals is that of Engels, who has shown that the following solution will give a satisfac-

¹ Classen and v. Reis, *Berichte*, 14, 1622.

tory result. The solution is designed with a view to the prevention of any precipitation of stannic oxide during the electrolysis. He takes 0.30 gram of the tin, as sulphate preferably, and adds 0.3 to 0.5 gram hydroxylamine sulphate or hydrochloride, 2 grams of tartaric acid, and 2 c.c. of ammonium acetate in 150 c.c. This he electrolyses at a temperature of 60° or 70° C. with a current density of 0.7 to 1.0 and E.M.F. 4.2 to 5.6 volts.

To test for the completeness of the deposition, withdraw some of the solution. If the deposition is taking place from the sulphide solution, acidify the extracted portion with sulphuric acid. A precipitation of stannic or stannous sulphide indicates that some tin is still present. In the case of the oxalate deposit, the free hydrochloric acid must be removed by ammonium acetate, a little free acetic acid added and a stream of hydrogen sulphide passed through. The deposit of tin is not at all easy to remove. If hydrochloric acid is used the solution must be boiled, whilst nitric acid oxidises the deposit. The best way is to cover the deposit with sulphuric acid and for the platinum anode used in the estimation substitute a German silver or copper wire, then reverse the current, making the deposit the anode. A very few minutes will suffice to clear this away from the platinum.

CHAPTER IX

ARSENIC

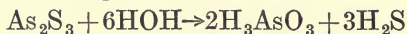
IN most of its chemical reactions arsenic functions as a metalloid ; it forms, *e.g.*, a gaseous hydride, acid anhydrides, and a chloride which exhibits the typical behaviour of acid chlorides towards water. The element forms two classes of stable compounds, the trivalent -ous and pentavalent -ic, of which the oxides As_4O_6 and As_2O_5 are important examples.

The trioxide As_4O_6 exists in two crystalline modifications and also in an amorphous form, all three of which are sparingly soluble in water—the amorphous variety is the most soluble of the three. The aqueous solution is regarded as a solution of arsenious acid, though the acid properties are feebler than those of a saturated aqueous solution of hydrogen sulphide. Nevertheless, the salts of arsenious acid are in many cases well characterised compounds, as, *e.g.*, the ortho-arsenites of silver and lead, Ag_3AsO_3 and $\text{Pb}_3(\text{AsO}_3)_2$, and the soluble crystalline potassium salt, which analyses out to the composition KAs_2O_4 . The rest of the arsenites, exclusive of those of the alkali metals, are insoluble or very sparingly soluble bodies of complex and frequently of inconstant composition—in fact, they should not be regarded in some cases as chemical compounds at all. This applies particularly to the so-called arsenites of iron, aluminium, and the earthy metals in general, obtained as precipitates by adding an excess of ammonia to a solution containing the metal and a soluble arsenite. The pentoxide is a white solid which can be melted without volatilisation by heating cautiously to low redness. At higher temperatures it decomposes into oxygen and the trioxide, which volatilises and may be sublimed. The solution of arsenic pentoxide in water is, at ordinary

temperatures, a solution of ortho-arsenic acid, H_3AsO_4 . At higher temperatures ortho-arsenic acid yields first of all pyroarsenic and afterwards metarsenic acid.

Arsenic does not form a pentachloride at ordinary temperatures. The trichloride AsCl_3 is a colourless oily liquid, boiling at 130°C ., which fumes in moist air like the analogous phosphorus trichloride, and for the same reason, viz. the formation of hydrochloric acid vapour. It mixes with water in all proportions, giving solutions which, when dilute, hydrolyse to arsenious and hydrochloric acids. The hydrolysis is arrested, of course, by hydrochloric acid, and as a matter of fact strongly acid solutions of the trichloride when heated evolve the undissociated chloride as a vapour. Similarly, when a mixed current of hydrogen sulphide and hydrogen chloride is passed through strong hot hydrochloric acid solutions of trivalent arsenic, no precipitate of trisulphide is obtained at all, but a removal of arsenic trichloride as vapour from the solution.¹

Three sulphides of arsenic are known. Of these the naturally occurring variety, As_2S_2 , realgar, is of no analytical importance. The trisulphide, which also occurs in a crystalline form in nature, is precipitated from arsenious solutions by sulphuretted hydrogen as a flocculent amorphous precipitate, which undergoes a change into the crystalline condition by prolonged shaking with acidified water. Precipitated arsenic trisulphide forms colloidal solutions with water, from which hydrogels can be separated by the addition of acids or salts or by warming. The solubility of As_2S_3 in pure water has been investigated by Schulze,² Linder and Picton,³ Winter⁴ and others—Schulze obtained a hydrosol with a sulphide content exceeding 37 per cent. Long continued boiling of precipitated arsenic trisulphide with a large excess of water results in perfect hydrolysis and solution according to the reaction



¹ Piloty and Stock, *Berichte*, 30, 1645.

² Schulze, *Journ. f. prakt. Chem.*, 25, 431.

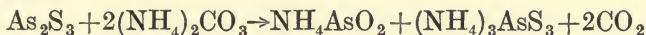
³ Linder and Picton, *Journ. Chem. Soc.*, 67, 63; 87, 1907.

⁴ Winter, *Zeit. f. anorg. Chem.*, 43, 228.

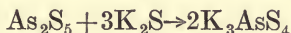
The determination of arsenic in steels and pig-irons, as well as in non-ferrous alloys by a method which embodies this reaction, is extensively practised. Arsenic trisulphide is not soluble in non-oxidising acids, but it dissolves freely in nitric acid, forming a mixture of arsenic and sulphuric acids. With caustic alkalis it yields soluble arsenites and thioarsenites.



It is freely soluble also in alkaline sulphides giving a solution of thioarsenite. Of some importance analytically is its solubility in ammonium carbonate solution according to the reaction



Arsenic pentasulphide, As_2S_5 , does not occur in nature. It can be precipitated by sulphuretted hydrogen under certain conditions (*vide infra*), or by acidification of thioarsenate solutions, as a yellow solid somewhat paler in colour than the trisulphide, which it resembles very closely in properties. It dissolves in alkaline sulphides forming thioarsenates,



and in alkaline hydroxides forming arsenates and, according to M'Cay, thioxyarsenates.



Alloys of arsenic are usually decomposed by oxidising acids or mixtures. Nitric acid of specific gravity 1.3, aqua regia, hydrochloric acid and potassium chlorate, &c., are all satisfactory and yield arsenic acid. It must not be forgotten that when hydrochloric acid is a constituent of the attacking mixture, a sufficient excess of the oxidant must be provided to make certain that no loss of arsenic as the trichloride occurs. Non-oxidising acids do not attack arsenic and its alloys as a rule, but the addition of a strip of zinc or iron often results in rapid decomposition, much of the arsenic being evolved as the gaseous hydride.

Solutions of trivalent arsenic are readily changed to the higher state of oxidation by the usual oxidants, but a feeble

agent like iodine is not effective in acid solutions. Conversely, the change from the pentavalent to the trivalent condition occurs, as a rule, only in the presence of free acid. In this connection the Bettendorff arsenic test, dating back to 1863, is worthy of mention. This consists in the addition of a solution of stannous chloride, made strongly acid with hydrochloric acid, to the liquid to be tested, when arsenic, if present, separates in the metallic form after some time as a brownish-black sediment. Traces of arsenic are revealed by a colouration only. The reaction does not take place unless the acidity exceeds that of 1.10 specific gravity.

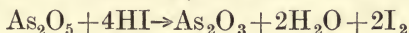
Arsenic is generally determined gravimetrically by weighing either as a sulphide or as magnesium pyroarsenate. Both the tri- and the pentasulphides are requisitioned for this purpose, and whereas formerly the determination was always made from trivalent arsenic solutions, numerous investigations have shown that the pentasulphide can also be secured by precipitation with sulphuretted hydrogen and, according to some, lends itself more readily to the subsequent operations of filtering and washing. Many analysts regard the precipitation of arsenic as a sulphide only as a means of removing the element from solution, and prefer to convert the sulphide into magnesium ammonium arsenate. The latter form of precipitation, due to Levöl and Rose, is effected from strongly ammoniacal solutions of pentavalent arsenic by means of "magnesia mixture." A correction, which is variously stated, for the solubility of the precipitate is generally introduced, but is, in the authors' opinion, unnecessary. The precipitate yields pyroarsenate on ignition. Gravimetric methods of minor importance include the precipitation as silver arsenate, the precipitation and determination as bismuth arsenate, $\text{BiAsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$,¹ and the precipitation as ammonium uranyl arsenate followed by ignition to the pyroarsenate $(\text{UO}_2)_2\text{As}_2\text{O}_7$.²

Volumetric methods are numerous, as one would expect from the ease with which the one state of oxidation of arsenic

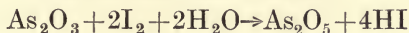
¹ Carnot, *Compt. Rend.*, 121, 20.

² Werther, *Journ. f. prakt. Chem.*, 43, 346; Puller, *Zeit. f. anal. Chem.*, 10, 72.

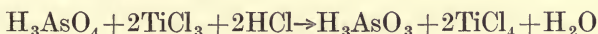
solutions can be reached from the other. The most common volumetric method is iodimetric, and one may either titrate the iodine liberated by the addition of an excess of potassium iodide to an acid solution of pentavalent arsenic according to



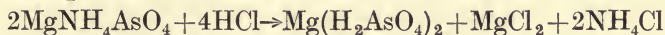
or, conversely, measure the iodine used in the oxidation from the tri- to the pentavalent condition in a solution made alkaline with sodium bicarbonate.



For the titration of acid solutions such reagents as potassium bichromate and potassium permanganate have been used for more than forty years, whilst potassium bromate, recommended by Györy,¹ is very largely used at the present time. This method is fully described under the determination of antimony. Of minor importance is the titration of a cold hydrochloric acid solution of pentavalent arsenic with a standard solution of titanium trichloride, according to Knecht and Hibbert.²



Of the volumetric methods which are based upon precipitations, the titration of ammonium magnesium arsenate by means of a standard solution of hydrochloric acid, according to the equation



is not much practised. The precipitation of a neutral arsenate solution by means of silver nitrate followed either by a determination of the excess of silver used or of that in the precipitate after dissolving, using the well-known Volhard method in either case, is much more common, and gives good results.

Arsenic does not lend itself to electrolytic determination. From hydrochloric acid solutions the arsenic is evolved as the hydride at the kathode, and depositions from oxalic acid solution or from solutions of the sulpho-salts are generally incomplete.

¹ Györy, *Zeit. f. anal. Chem.*, 32, 415.

² Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis*.

Gravimetric Determination.

(A) *Determination as Trisulphide.*—Arsenic is quantitatively precipitated by hydrogen sulphide from its trivalent solutions of any degree of acidity at the ordinary room temperature, and from warm solutions of 5N acid strength the precipitation is quantitative at 70° C., a fact which is of some importance in connection with the separation of arsenic from antimony and tin. From hotter solutions there is danger of loss by volatilisation as trichloride. The older text-books and some modern ones recommend, for purposes of estimation by weighing as trisulphide, after passing hydrogen sulphide to saturation through a cold and strongly acid solution, that the excess of the reagent should be removed by a current of carbon dioxide. Rose, for example, states that small quantities of sulphide remain dissolved in solutions saturated with hydrogen sulphide, but this was shown by Ward¹ to be untrue, and that the passage of carbon dioxide was not only unnecessary but dangerous, as leading to slight decomposition of the trisulphide. Washing with *hot* water is also harmful on account of its hydrolytic action on the precipitate.

The outstanding feature of the determination of arsenic as trisulphide is the fact that the results are apt to err on the positive side. The determination of the cause of this plus error has attracted the attention of many observers: Friedheim and Michaelis, Leher, Baumann amongst others. The excess of sulphide found over that known to be present was attributed by some to the presence of a "sulphydrate" in the precipitate, and this led to several recommendations for its removal. Baumann,² for example, states that the plus error varies from 0.35 per cent. in 3N hydrochloric acid solutions, to 4 per cent. in 12N, and is accompanied by a corresponding decrease in the colour intensity from orange to a yellow as pale as that of the pentasulphide. He removes the sulphydrate by repeated washings with hot

¹ *Jahresberichte d. Chem.* (1873), 235.

² *Dissert.*, München, 1907.

alcohol. The same observer found, however, and this has been subsequently confirmed by various operators, that the washed precipitate invariably contains chlorine in some form, and its amount also increases with the acidity of the solution from which the precipitation was made. An exhaustive investigation of the whole subject by Freitag¹ led him to reject the "sulphydrate" hypothesis, and he concluded that chlorine, not removable by prolonged washing with hot alcohol, is the cause of the positive error. The solution of the difficulty is found in a lowering of the acid strength to that of unit normality, or in a substitution of sulphuric for hydrochloric acid solutions. The process therefore becomes, so far as pure solutions of trivalent arsenic are concerned, the following.

The acidity of the solution must be adjusted to normal strength in the case of hydrochloric acid, or to about six times normal strength of sulphuric acid, and the solution must be free from any oxidant. A rapid stream of hydrogen sulphide is passed through the solution for half an hour at the temperature of the laboratory, and the liquid then allowed to stand for ten minutes for settling. The clear liquid is decanted as far as possible from the precipitate and poured through a filter contained in a Gooch crucible. The precipitate is finally transferred to the filter and washed thoroughly with cold water only. It is dried as well as may be by suction at the filter pump and finally to constant weight at 85° C. in an atmosphere of carbon dioxide.

Wt. of $\text{As}_2\text{S}_3 \times 0.6091 = \text{wt. of arsenic.}$

(B) *Determination as Pentasulphide.*—The determination of arsenic as pentasulphide has been practised for a long time; Bunsen,² e.g., passes hydrogen sulphide through hot arsenate solutions to saturation, allowing the solution to cool during the process, sets aside in a warm place for a day, filters, washes with alcohol and carbon disulphide, and dries at 110° C. No special importance was apparently attached to the concentration of the solution with respect to hydrochloric acid, which was found subsequently, however, to

¹ *Dissert.*, München, 1910.

² *Annalen*, 192, 319.

exert a pronounced effect on the composition of the precipitate. The instability of pentavalent arsenic solutions in the presence of strong hydrochloric acid, and the reducing action of sulphuretted hydrogen, may lead to a precipitation of arsenic trisulphide and sulphur along with the pentasulphide under certain circumstances. In general terms, it may be stated that the amount of pentasulphide increases with increasing amounts of acid and falling temperature, and conversely, the amount of trisulphide with decreasing acid and rising temperature.¹ Numerous investigations have been made from time to time of this subject, and the various recommendations are somewhat conflicting. Thiele,² *e.g.*, puts it on record that a rapid stream of sulphuretted hydrogen precipitates a mixture of sulphur with trisulphide and pentasulphide from concentrated hydrochloric acid solutions in the cold, which is not in agreement with the preceding. M'Cay³ obtains a perfect precipitation of the pentasulphide from a strongly acid solution of an alkaline arsenate by saturating with sulphuretted hydrogen, and heating the saturated solution, contained in a tightly-closed vessel, in the water bath at 100° C. for an hour.

Fr. Neher's modification⁴ of the Bunsen method is as follows. The solution of the arsenate should contain one part of water and at least two parts by volume of concentrated hydrochloric acid, thus giving approximately an 8N acid solution, and a rapid and uninterrupted stream of pure hydrogen sulphide passed through it to complete saturation. The solution must be kept cool throughout; even the rise in temperature occasioned by mixing the original aqueous solution with twice its volume of strong hydrochloric acid must be prevented by external cooling during the operation. The precipitation does not begin at once, the solution remaining clear and colourless for quite a time. The first visible effect is the production of a green colour which is followed almost immediately by a turbidity, then by a finely divided white precipitate, and lastly by pale yellow arsenic pentasulphide in flocks. Filtration is rapid

¹ Brauner and Tomicek, *Jour. Chem. Soc.*, 87 (1905), 1370.

² *Annalen*, 265, 65. ³ *Zeit. anal. Chem.*, 26, 635. ⁴ *Zeit. anal. Chem.*, 32, 45.

and so also is the washing, which is done first with water and afterwards with hot alcohol to eliminate traces of sulphur. The precipitate is dried at 100° C. to constant weight.

The method just described did not yield good results in the hands of Leher (*Diss.*, 1904), who obtained incomplete precipitation from 8N acid solutions after passing hydrogen sulphide for as long a time as two hours, and allowing to stand afterwards in a tightly-closed vessel for a long time. The precipitates, moreover, were very fine and difficult to retain on the filter. Good results were obtained by passing a rapid current of hydrogen sulphide through the arsenate solution containing one-third of the total volume of strong acid. The solution was maintained constantly at 70° C. for an hour and then allowed to cool for a further 15 minutes without interruption of the current. The precipitate was washed with 30 per cent. hydrochloric acid previously saturated with sulphuretted hydrogen and afterwards with hot alcohol, and finally dried at 110° C. The preceding sketch by no means exhausts the number of contributions to this subject; amongst others, those of Pilotý and Stock,¹ Virgili,² Usher and Travers,³ Jannasch and Hiemann,⁴ and Erdmann,⁵ are particularly worthy of note. The causes of the many contradictions which occur in the literature are difficult to find, but the exhaustive and excellent thesis of Freitag, previously cited, throws much light on the matter, as the following facts, experimentally determined, show.

1. Arsenic pentasulphide precipitated from solutions containing hydrochloric acid contains chlorine, the amount of which, as in the case of the trisulphide, increases with the acid concentration.

2. Whereas the trisulphide is practically completely insoluble in cold water, the pentasulphide has a very slight solubility. Hot water hydrolyses both sulphides, and hot alcohol dissolves both to a slight extent.

3. Drying in an air bath leads to oxidation in both cases, and an indifferent atmosphere must be employed. Above

¹ *Berichte*, 30, 2, 1655.

² *Zeit. f. anal. Chem.*, 44, 492.

³ *Journ. Chem. Soc.*, 87, 1370.

⁴ *Journ. f. prakt. Chem.*, 74, 473.

⁵ *Lehrbuch der anorg. Chem.* (1906).

90° C. the pentasulphide decomposes into trisulphide and sulphur and the latter is in part volatilised, leading to low results.

4. Loss of arsenic at 70° C. only occurs when the acid strength is 9N.

5. The precipitation as pentasulphide is made more certain by increase of acid concentration, also of temperature and speed of hydrogen sulphide current. The first two of these factors operate disadvantageously in other directions, *e.g.* see 1 and 4.

The best method, based on the above facts, is the following. The solution, containing all the arsenic in the pentavalent form and no other oxidising substance, is brought to 6N acidity with hydrochloric acid and heated to 70° C. A rapid stream (750 c.c. per minute) of hydrogen sulphide is passed through the solution for 20 minutes, the temperature being kept constant. If the concentration of the solution with respect to arsenic is not too small, and the current of gas is maintained uninterruptedly, the time specified is ample for complete precipitation. The precipitate is filtered whilst still hot through a weighed Gooch crucible, and washed with cold water until the washings do not react with silver nitrate solution. It is then sucked as dry as possible at the pump, and finally dried to constant weight at 90° C. in an atmosphere of carbon dioxide.

Wt. of $\text{As}_2\text{S}_5 \times 0.4832 = \text{wt. of arsenic.}$

(C) *Determination as Magnesium Pyroarsenate.*—The present text-book form of the determination of arsenic by precipitation with “magnesia mixture,” which was originated by Levöl,¹ differs from the original recommendations in many respects, sources of error having been eliminated as the result of many investigations since that time. The following is typical of the modern method.

The solution containing arsenic acid or a soluble arsenate is concentrated to as small a volume as possible, and for every 50 c.c. of it there are added 10 c.c. of binormal ammonium chloride solution and 20 c.c. of the “magnesia

¹ Levöl, *Ann. Chim. Phys.* (3), 17 (1846), 501.

mixture," the latter being added in drops to the solution, which is swirled all the time. After some time a further addition of 10 per cent. ammonia, amounting to about one-third the volume of the solution, is made, and the mixture then allowed to stand overnight. The crystalline precipitate is collected on asbestos in a Gooch crucible, washed with $2\frac{1}{2}$ per cent. ammonia until free from chloride, and dried quickly in the air bath at about 110° C. The crucible is then placed inside a larger one, Fig. 21, and the temperature very slowly raised to that of bright redness, at which it is maintained for at least 15 minutes. The residue is magnesium pyroarsenate, $\text{Mg}_2\text{As}_2\text{O}_7$, and contains 48.27 per cent. of arsenic. The magnesia mixture is made by dissolving 55 grams of magnesium chloride crystals, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and 70 grams of ammonium chloride in 650 c.c. of water, and making up to a litre with ammonia of specific gravity 0.96. The magnesia mixture was originally made up from the sulphate, but this was soon discarded because the precipitate was found to be contaminated with basic magnesium sulphate.

The solubility of ammonium magnesium arsenate is about 1 in 600 of water, hence the addition of ammonia, which lowers the solubility to 1 in about 24,500, according to Virgili.¹ The same end is secured by some workers by the addition of alcohol, though this might result in the precipitation of magnesium salts if used too liberally. Rose recommended its addition to the extent of one-fourth the volume of the solution. Others make use of a correction for the solubility of the precipitate. Puller,² for example, adds to the weight of $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ one milligram per 30 c.c. of filtrate, and Ducru³ adds the same amount to the weight of the anhydrous precipitate for each 50 c.c. of filtrate. Dried at 100° to 102° C., the precipitate is approximately $\text{MgNH}_4\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, and it is not quite anhydrous at 110° C., hence the ignition to pyroarsenate. If the ignition be conducted over a Bunsen flame, great care must be taken

¹ Virgili, *Zeit. f. anal. Chem.*, 44, 504.

² Puller, *Zeit. f. anal. Chem.*, 10, 53.

³ Ducru, *Bull. Soc. Chim.* (3), 23, 904.

to exclude reducing gases. Besides covering with a lid, some workers add ammonium nitrate before commencing the ignition, which, above all, must be conducted slowly. The authors prefer to ignite in a muffle furnace, commencing at or near the mouth, and gradually pushing the crucibles towards the back.

One of the most recent contributions to the subject is that of Austin, in which the low results due to reduction by ammonia during ignition (Rose, Reichel, Rammelsberg, &c.), or to the solubility of the precipitate in ammoniacal water or salts of ammonia, are eliminated by the following procedure, which has given excellent results in the authors' hands.

The slightly acid solution of the arsenate, containing no ammonium salts if possible, is added drop by drop to the magnesia mixture, which is faintly but distinctly alkaline. A few drops of concentrated ammonia are then added, and as soon as the precipitate subsides, filtration is at once proceeded with, a Gooch crucible and asbestos filter being used. Particles of precipitate adhering to the beaker are removed by means of portions of the filtrate and a "policeman," and the washing is done with 25 c.c. of water made faintly ammoniacal, added a little at a time. Drying and ignition are conducted cautiously as before.

If no ammonium salts are present in the original solution, an excess of 30 c.c. of magnesia mixture is ample in a total volume of 200 c.c. If ammonium salts are present the amount of magnesia mixture must be considerably increased, 150 c.c. being recommended. Gooch and Phelps¹ use the method for very small quantities of arsenic as well as for large amounts, and they freeze the mixture after addition of the precipitant, filtering after allowing it to melt at the temperature of the laboratory.

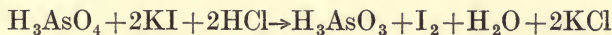
The magnesia mixture for this excellent process is made by dissolving 110 grams of magnesium chloride crystals in water, adding also 58 grams of ammonium chloride, filtering and making up to two litres with water and 10 c.c. only of strong ammonia.

¹ Gooch and Phelps, *Amer. Journ. Sci.*, xxii. 492.

(D) *Determination as Silver Arsenate* (Pearce).¹—This method depends upon the precipitation of silver arsenate by means of silver nitrate. The solution of the arsenate, free, of course, from halogen compounds, is made nearly neutral if originally acid, by means of ammonia, and an excess of silver nitrate solution is then added. The liquid is then made exactly neutral by very dilute ammonia, and the mixture kept warm for some time. The chocolate-brown precipitate quickly settles, and is then filtered through asbestos in a Gooch crucible, washed with hot water until the washings are free from silver, dried at 100° C., and weighed as Ag_3AsO_4 , containing 16.21 per cent. of arsenic.

Volumetric Determination

(A) *Iodimetric Method*.—An iodimetric method can be applied either to pentavalent or trivalent arsenic solutions. In the former case an excess of potassium iodide is added to the arsenic solution, which must be acid, whereupon iodine is liberated:



It is found that a direct titration of the liberated iodine with sodium thiosulphate yields low results, averaging three milligrams of iodine for two decigrams of arsenic present. It is better, therefore, as Gooch and Browning recommend, to distil the iodine out of the reaction mixture before titrating. The method is not of much practical importance.

The much better known process of Mohr is the converse of the preceding, and is worked almost exactly as described for antimony, which metal must therefore be absent from the solution. This applies also to stannous solutions. If the original arsenious solution is alkaline, it is made just acid; if it is strongly acid, the excess of acid must be removed or neutralised. The feebly acid solution is now treated with 20 c.c. of a saturated solution of sodium bicarbonate, which must be free from normal carbonate and

¹ Pearce, *Dingler's Polyt. Journ.*, 249, 523; 250, 475.

from caustic soda, both of which react with iodine. (Alkalinity is necessary to remove the hydriodic acid from the reaction mixture and thus determine the reversible reaction $\text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_4 + 2\text{HI}$, in the direction of the arrow to completion). After adding starch solution, decinormal iodine is run in from a burette until the blue iodide of starch is formed. Some chemists prefer to add an excess of a few drops of iodine after the appearance of the blue colour, and titrate back again with a standard solution of sodium thiosulphate. Each c.c. of $\frac{\text{N}}{10}$ iodine is equivalent to 3.75 milligrams of arsenic.

(B) *Adaptation of Silver Arsenate Method.*—The arsenic existing in the pentavalent forms in a feebly acid solution is precipitated with an excess of silver nitrate exactly as described under the gravimetric determination. A complete precipitation in the form of silver arsenate is also obtained by adding to the faintly acid solution 10 c.c. of ammonium acetate and 10 c.c. of acetic acid B.P., warming, and then adding the silver nitrate solution. The chocolate-brown arsenate of silver is allowed to settle by digesting in a warm place for a short time, and is then filtered and washed with water containing a little ammonium acetate. The precipitate is then dissolved from the filter with 10 per cent. nitric acid, and the silver in solution titrated by the ordinary Volhard method of adding a few drops of a strong solution of ferric-alum, and then running in a standard solution of ammonium thiocyanate until the liquid shows the red colour of ferric thiocyanate to be permanent. The thiocyanate solution is standardised empirically against a solution of silver nitrate of known strength. A convenient strength of ammonium thiocyanate solution is approximately $\frac{\text{N}}{50}$ (1.5 gram per litre). One gram of silver is equivalent to 0.231 gram of arsenic.

(C) *Adaptation of Bettendorff Reaction.*—This well-known reaction was used by Andrews and Farr¹ for the quantita-

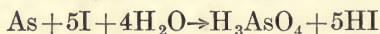
¹ Andrews and Farr, *Zeit. f. anorg. Chem.*, 62, 123.

tive determination of small quantities of arsenic, ranging from 0.0001 gram to 0.1 gram. The authors have tested it thoroughly, and find it a most excellent method for the determination of the small quantities of arsenic unavoidably present in many alloys, white metals in particular.

If a strongly acid solution of stannous chloride is added to a solution containing arsenic, a brownish-black precipitate forms, which is very finely divided, but settles in process of time. It consists, according to Bettendorff, of metallic arsenic to the extent of 95.86 to 98.56 per cent., the remainder being constituted of tin in some form or other. There seems to be little doubt, however, that the tin, which exists probably as a basic chloride, varies within wider limits than these; the actual amount is conditioned by the degree of oxidation of the stannous chloride reagent, temperature, and other circumstances. The precipitate can be readily collected on an asbestos filter, and washed, first with concentrated hydrochloric acid and then with water, without undergoing oxidation. It dissolves in a solution of iodine in potassium iodide at a rate which is greater, the smaller the amount of tin in it, a circumstance which suggested to Andrews and Farr the introduction of tartaric acid into the reagent. They found that the deposit is then free from tin; they also showed that with 23 per cent. of free hydrochloric acid in the reagent, the complete precipitation of the arsenic required a long time, but with 25 per cent. only a few minutes. They therefore recommended the addition of about 30 per cent. of acid to the solution, of which latter at least 25 c.c. should be used for each 10 c.c. of solution to be tested. There is no danger of loss of arsenic at temperatures below 40° C., but it is not advisable to employ temperatures below 25° C., otherwise the action is too slow.

The Process.—The neutral trivalent arsenic solution, contained in a flask provided with a stopper, is treated with $2\frac{1}{2}$ times its own volume of the reagent mixture, the stopper inserted, and the mixture kept at or about 40° C. for two or three hours. The deposited arsenic is filtered through asbestos, using concentrated acid to transfer from the flask and also for washing. Small quantities of water are used

for the final washing. A measured excess of standard iodine solution is then delivered from a burette into the flask, and shaken round in order to dissolve any adherent film of arsenic, and the solution is then poured over the filter so as to dissolve off the precipitate. An insufficiency of the iodine solution is indicated by the complete loss of colour. The solution and washings are caught in a flask, the liquid made distinctly alkaline with a 5 per cent. solution of sodium bicarbonate, and the excess of iodine titrated with standard arsenic solution. The interaction between finely divided arsenic and iodine may be written thus :



In the presence of sodium bicarbonate, thus :



The strength of the standard solutions used depends upon the amount of arsenic to be determined. For ordinary alloys to which arsenic has not been purposely added, centinormal solutions will be found most useful. For amounts of arsenic less than 0.0005 gram, $\frac{\text{N}}{1000}$ iodine is used, but it is necessary to deduct 0.6 c.c. from the total amount used, since it requires so much to strike a colour with the starch. Decinormal iodine is suitable for amounts of arsenic ranging from 10 to 100 milligrams.

The reagent is made by dissolving 20 grams of stannous chloride crystals and 40 grams of tartaric acid in 1 litre of 40 per cent. hydrochloric acid. The solution should be kept in a number of small bottles, filled up to the stoppers.

The method is valuable on account of the wide range of its applicability—it is not even necessary to remove antimony and lead from the solution, if present.

The authors are of opinion that the time allowed for the precipitation of the arsenic is not sufficient in many cases. They prefer to allow at least twenty-four hours in a warm place during the day and in the cold overnight. If it is possible to allow forty hours, so much the better. This constitutes a drawback to what is in all other respects a most excellent method.

CHAPTER X

ARSENIC, ANTIMONY AND TIN SEPARATIONS

THE occurrence of antimony and tin in such a large number of commercial alloys accounts to a large extent for the number of methods now available for the separation of these two metals. Arsenic, too, exists in most alloys, generally as an impurity, and the necessity for its determination has also resulted in the production of methods for separating it not only from lead, copper, &c., but also from antimony and tin.

The method most commonly used for the separation of arsenic from other metals is based on the insolubility of its sulphides in highly concentrated hydrochloric acid solutions, and is therefore capable of extensive application. The separation, however, is seldom quantitative, as precipitated arsenic sulphide exhibits a strong adsorptive effect ; *e.g.* the easily soluble sulphides of tin and zinc, singularly enough, are almost invariably to be found in arsenic sulphide precipitated from solutions containing these metals. As a means of concentrating the whole of the arsenic into the compass of a small precipitate, the process is, nevertheless, very valuable in the analysis of metals and alloys.

Capable of even greater generality of application is the "distillation method," based upon the volatility of arsenic trichloride, though the process is not so frequently practised in this country as abroad. The precipitation of arsenic (As^v) as magnesium ammonium arsenate is also often used in separating the element from antimony (and tin), particularly in alkaline tartrate solutions. In connection with the analysis of cupriferous alloys, the adsorptive properties of freshly precipitated colloids such as ferric and aluminic hydroxides provide a further useful method for the separation of small amounts of arsenic. Of minor importance is

the removal of arsenic from solutions in the form of the gaseous hydride; this method is suited to electrolytic depositions.

The older methods of separating antimony from tin include the precipitation of the former as metal by means of other metals such as iron,¹ and the method of Rose,² based upon the insolubility of sodium antimonate in alcohol. Quite a number of separations of antimony from tin are based upon the difference in the solubilities of their sulphides. These include the precipitation from oxalic acid solution, introduced by Clark,³ and modified considerably of recent years by Ratner,⁴ Rossing,⁵ and Henz⁶; the Vortmann-Metzl⁷ precipitation from phosphoric acid solutions, the precipitation from hydrofluoric acid solutions, due to M'Cay,⁸ and the precipitation from hydrochloric acid solutions of definite concentration (Panajotow,⁹ Scharer,¹⁰ &c.). The last of these have already been dealt with in Chapter III.

Electrolytic separations, of which Classen¹¹ laid the foundations, are also extensively used at the present time.

The scope of this work excludes the description of many of the separation methods alluded to above, and those only which are, in the authors' opinion, best suited to the needs of the student or works' chemist are appended.

Separation of Arsenic from Antimony and Tin

(a) *Sulphuretted Hydrogen Method—Separation from Antimony only.*—The metals are supposed to exist in the higher state of oxidation in hydrochloric acid solution. In

¹ Tookey, *Journ. Chem. Soc.*, 15 (1862), 462.

² *Ann. Chem.*, 64 (1847), 404.

³ *Chem. News*, 21 (1869), 124.

⁴ *Chem. Zeit.*, 26 (1902), 873.

⁵ *Zeit. f. anal. Chem.*, 41 (1902), 8.

⁶ *Zeit. f. anorg. Chem.*, 36 (1903), 46.

⁷ *Zeit. f. anal. Chem.*, 44 (1905), 525.

⁸ *Journ. Amer. Chem. Soc.*, 31 (1909), 373.

⁹ *Berichte*, 42 (1909), 1496.

¹⁰ *Dissert.*, München, 1911.

¹¹ *Berichte*, 14 (1881), 1622; 17 (1884), 2462; 18 (1885), 1104.

the ordinary course of analysis they are frequently obtained as a precipitate of the mixed trisulphides. This, whilst wet, is dissolved in a solution of 3 per cent. caustic potash, and a current of chlorine gas is then conducted through the liquid until the excess of alkali is decomposed. The solution, which now contains some potassium chlorate, is warmed and treated with concentrated hydrochloric acid, drop by drop, until the chlorate is decomposed, and the liquid concentrated by evaporation. It is then free from excess of chlorine, and, after cooling in ice, is treated with twice its volume of ice-cold concentrated hydrochloric acid. A rapid current of sulphuretted hydrogen is then passed through the solution for about an hour, the vessel closed and allowed to stand for some time, and the arsenic pentasulphide collected on asbestos. The precipitate is washed with a mixture of 2 volumes concentrated hydrochloric acid with one of water, until sulphuretted hydrogen yields no precipitate with the largely diluted washings. The final determination of the arsenic is best made from a solution of the precipitate in concentrated nitric acid or alkaline hydrogen peroxide, by one of the methods previously described.

The antimony is obtained from the filtrate as a precipitate of pentasulphide by diluting very largely with water and passing more sulphuretted hydrogen through the solution. The final determination in this case also, is best made by one of the volumetric methods.

(b) *The Distillation Method—Separation from most Metals.*—This method constitutes a means of separating arsenic from tin as well as from antimony.

The solution, measuring about 200 c.c., should contain 25 per cent. of hydrochloric acid; aqueous solutions are therefore brought up to this degree of acidity by the addition of concentrated hydrochloric acid, or by passing a current of the gas into them. The arsenic must be present in the lower state of oxidation, so that if obtained in the pentavalent form by dissolving the previously precipitated trisulphide in hydrochloric acid and chlorine, (or potassium chlorate) or in alkaline hydrogen peroxide, a reducing agent must be

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introduced. E. Fischer,¹ to whom the method is due, used ferrous chloride, Classen² substituted ferrous ammonium sulphate, and at the present time potassium bromide is most commonly used. It suffices in most cases to continue the distillation until the volume of liquid in the flask is reduced to about one-third of the original amount, but if arsenic is then not completely removed, as shown by testing a sample of the distillate with sulphuretted hydrogen, more concentrated acid is added and the distillation continued. The distillate is free from antimony and tin if the temperature of the boiling mixture does not at any time exceed 110° C. Fischer found it necessary to prevent this, when the bulk of the liquid became too small, by the addition of hydrochloric, often repeated two or three times. Other means consisted in the passage of a current of hydrochloric acid gas, or of a mixture of it with sulphur dioxide, during the distillation, a procedure which is still largely used and advocated. The difficulty was overcome by Hofmann³ by distilling from a mixture in 20 per cent. acid of 12 grams of potassium chloride with 5 grams of ferrous chloride. The boiling point of such a solution never reaches 110° C. before absolute dryness is reached, and no repetition of the distillation is necessary. The amounts of reagent specified were used in the separation of 0.3 gram of arsenic from 0.5 gram of antimony.

One of the most recent modifications of the distillation is due to Jannasch, who utilises the reducing properties of hydrazine. The solution containing the arsenic and other metals in a small volume of water and hydrochloric acid, is introduced into the distillation flask and diluted to about 100 c.c. with fuming hydrochloric acid. After adding 3 grams of hydrochloride or sulphate of hydrazine and 1 gram of potassium bromide, or their equivalent in the form of 3 grams of hydrazine hydrobromide alone, the mixture is distilled as rapidly as possible to a bulk of about 30 c.c. The process, occupying about one hour, results in the com-

¹ *Ann. Chem.*, 208 (1881), 182.

² *Berichte*, 18 (1885), 1110.

³ *Dissert.*, Berlin, 1911.

plete removal of the arsenic, whilst antimony, tin, copper, lead, and bismuth remain behind. The excess of hydrazine salts in the flask is decomposed by nitric acid before the determination of tin or antimony is attempted. The arsenic in the distillate, if sufficiently large in amount, is determined directly by titration with potassium bromate or iodine. Smaller quantities are first separated as sulphide.

The distillation apparatus needs no separate description. It is important, however, to provide efficient cooling so as to prevent loss of traces of arsenic; a water-jacketed glass worm answers the purpose admirably. Bumping is prevented by the introduction of broken glass or porcelain. The reagents must necessarily be free from arsenic; the acid in particular should be carefully tested by the stannous chloride reaction.

(c) *Precipitation from Tartrate Solutions—Separation from Antimony and Tin.*—The precipitated sulphides are dissolved by means of a solution of caustic potash and a current of chlorine gas, and the excess of chlorine removed as before by the addition of hydrochloric acid. The acid solution is then treated with tartaric acid and the solution made alkaline with ammonia. If no precipitate is formed, sufficient tartaric acid has been added; in the other event, the precipitate is allowed to settle, and the clear liquid decanted. The precipitate is then dissolved in more tartaric acid solution and the two liquids combined. The arsenic is then precipitated with magnesia mixture in the manner fully described on p. 120. The precipitate is usually contaminated with small amounts of basic magnesium tartrate, particularly if the quantity of arsenic is considerable. It is therefore dissolved in hydrochloric acid, and the precipitation repeated.

The separation from antimony by the above method is perfect, though the operations are tedious; in the case of tin, no deviation from the procedure is necessary beyond the addition of much larger quantities of tartaric acid.

Separation of Tin and Antimony

(a) *Precipitation from Solutions containing Hydrofluoric Acid.*—For this separation, the metals should exist in the higher state of oxidation in hydrochloric acid solution. This condition can be produced from a precipitate of the mixed sulphides by the usual operations.

The solution, reduced to as small a bulk as possible, is treated with an excess of a solution of tartaric acid and then neutralised with sodium hydrate. A solution of 48 per cent. hydrofluoric acid is then added, and this is followed by an excess of sodium acetate. After diluting largely with water, the antimony is precipitated by a current of sulphuretted hydrogen; the tin remains in solution. The determination of the antimony then proceeds along the usual lines. The filtrate is evaporated in a platinum dish, with the addition of sulphuric acid to expel hydrofluoric acid, the solution largely diluted with water, and the tin thrown out of solution as sulphide.

(b) *Precipitation from Solutions containing Phosphoric Acid.*—The mixed sulphides of antimony and tin are dissolved in hydrochloric acid, the sulphuretted hydrogen expelled from the solution, which is then neutralised by sodium hydrate and diluted to a volume of about 60 c.c. An equal volume of phosphoric acid solution of specific gravity 1.3, and 24 c.c. of concentrated hydrochloric acid are then added, and the liquid saturated at the boiling point with sulphuretted hydrogen. The black sulphide of antimony is then filtered out, and determined as such, or redissolved and the antimony determined volumetrically. The filtrate from the antimony sulphide is made nearly neutral, diluted with an equal volume of water, warmed, and the tin precipitated as sulphide and converted to oxide, or redissolved for volumetric determination of the metal.

(c) *Precipitation from Hydrochloric Acid Solution.*—The following are the recommendations of Panajotow for the separation of antimony and tin out of hydrochloric acid solutions; those of Scharrer have already been given.

The acidity of the solution is adjusted to 15 per cent. of hydrochloric acid, and the sulphuretted hydrogen passed in a rapid stream at a temperature of 50° to 60° C. for half an hour. The liquid is then allowed to cool to 30° C., and the current passed for some time longer and less rapidly. The precipitated antimony sulphide is collected in a Gooch crucible, washed with water containing sulphuretted hydrogen, and then successively with alcohol, carbon disulphide, and ether, before drying and weighing. The tin is precipitated, also as sulphide, after neutralising most of the acid with ammonia.

(d) *Precipitation from Oxalic Acid Solution.*—For this separation the tin must be present in solution in the quadrivalent form and is readily obtained in that form by dissolving the sulphides of tin and antimony in hydrochloric acid. The solution, according to Clark, should contain from 40 to 50 times the weight of tin present of oxalic acid, and even then the precipitate of antimony sulphide obtained by passing a current of sulphuretted hydrogen through the hot solution was not entirely free from tin, and a repetition of the precipitation was recommended. According to Rössing,¹ there is liability to loss of tin as volatile tetrachloride by dissolving stannic sulphide in hydrochloric acid, and he treats the sulphides of tin and antimony, or their solution, in an alkaline sulphide, directly with the oxalic acid. This procedure fails to yield a quantitative separation of the metals at one precipitation, according to Henz, and he modified the original method of Clark to the extent of adding to the oxalic acid solution a mixture of potassium oxalate and potassium tartrate, and found that one precipitation sufficed for a complete separation. The method finally recommended by Henz is as follows, and constitutes at the present time the standard procedure for this separation.

For every 3 decigrams of mixed tin and antimony in the solution, there are added 6 grams of caustic potash and 3 grams of tartaric acid, and an excess of hydrogen peroxide

¹ *Zeit. f. anal. Chem.*, 41 (1902), 8.

is then added until the yellow colour of the solution is completely dissipated. The solution is heated to boiling for a few minutes, in order to effect complete oxidation of thiosulphates. About 15 grams of oxalic acid are then added, and the liquid boiled for 10 minutes to decompose the excess of hydrogen peroxide. A rapid stream of hydrogen sulphide is then passed through the solution, which should occupy a volume of about 100 c.c., and be maintained at the boiling point. When the precipitation of antimony sulphide begins, which may not occur for 10 to 15 minutes, another 15 minutes are allowed before diluting with hot water to about 250 c.c. Fifteen minutes later the boiling is stopped, but the stream of gas continued for at least 10 minutes during the cooling. The last item is of importance, because small quantities of antimony remain unprecipitated at the boiling point of the mixture. Filtration through a Gooch crucible must be conducted as rapidly as possible. The precipitate is washed twice by decantation with a 1 per cent. solution of oxalic acid saturated with sulphuretted hydrogen, and then with very dilute acetic acid, similarly treated. The "wash" solutions are applied hot. The final determination of the antimony was made by Henz as sulphide in an atmosphere of carbon dioxide. The tin was determined by concentrating the filtrate, adding 5 c.c. of sulphuric acid (1 : 1) and electrolysing with a current of 0.3 ampere at a voltage of 2 to 3.

The electrolytic determination of tin in the filtrate is not satisfactory; Henz, *e.g.*, obtained results in his test analyses in the above method, which were low to the extent of about 1 per cent. Clark and Rössing determined the tin in the filtrate by neutralising the oxalic acid with ammonia, making acid with acetic acid, and precipitating with hydrogen sulphide. The stannic sulphide obtained from such solutions, however, is very voluminous and difficult to manipulate. Better results follow from a precipitation of the tin as metal by means of zinc, and subsequent volumetric determination.

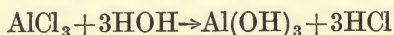
CHAPTER XI

ALUMINIUM AND CHROMIUM

Aluminium

ALUMINIUM belongs to the group of elements which do not form sulphides by the usual wet reactions, but which are precipitated as hydrated oxides by means of soluble hydroxyl compounds. The group includes also iron and chromium. Whilst, however, the literature of analytical chemistry is particularly rich in methods for the determination of iron and chromium, it is not swollen to any considerable extent by the chemistry of aluminium. In the first place the metal does not lend itself to electrolytic determination at all, and secondly, the volumetric methods are not only based on the precipitations employed in the gravimetric determination, but are also approximate only. The gravimetric methods are, essentially, only two in number, the first being the precipitation as hydroxide followed by ignition to alumina, and the second the determination as phosphate.

Salts of aluminium are very readily hydrolysed, so much so that an aqueous solution of a normal salt of aluminium usually exhibits an acid reaction. It is not difficult therefore to effect complete hydrolysis according to the reaction



Intermediate basic chlorides, the products of partial hydrolysis, also exist; this is the case also with ferric salts. Several hydrolytic agents have been employed to bring about the complete hydrolysis by neutralisation of the acid formed, the ordinary ammonia precipitation constituting an example. Other reagents are sodium thiosulphate, sodium or ammonium nitrite, and a mixture of potassium iodate with iodide.

Strong bases such as sodium hydroxide redissolve the

precipitate of aluminium hydroxide, which they yield at first, forming a solution of sodium aluminate from which the aluminium is completely thrown down by a current of carbon dioxide. The basic carbonate thus obtained possesses much better filtering properties than the hydroxide.

Aluminium hydroxide readily yields alumina on ignition at comparatively low as well as at high temperatures. If it is necessary to redissolve the ignited residue in hydrochloric acid (the usual solvent) for further analysis, it is important that the ignition should be conducted at low redness, since high temperatures yield products soluble only with difficulty or not at all.

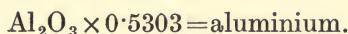
Aluminium hydroxide exists in a soluble (hydrosol) as well as an insoluble (hydrogel) form, and the change from the former to the latter is not completed by boiling except in the presence of foreign salts; hence the use of ammonium chloride in ammonia precipitations of aluminium. No useful purpose is served by protracted boiling, since ammonium salts under such treatment are liable to slight decomposition into volatile ammonia and free acid, which would redissolve small quantities of the precipitate. Before filtration it is always necessary, therefore, to assure oneself of slight alkalinity; this applies also to solutions that have been allowed to stand for a long time. Long boiling also results in contamination of the precipitate with small quantities of silica from glass vessels and, what is much worse, in slimy precipitates exceedingly difficult of filtration. The gelatinous character of precipitated aluminium hydroxide, and the slow filtration which it necessitates, have resulted in various devices to overcome them. Thus, coagulation is induced by such substances as tannin (Divine),¹ and glycerol (Guyard).² Liebermann uses starch for the same purpose, and Zulkowsky shakes the liquid precipitate with one-third its volume of ether.

¹ Divine, *Journ. Soc. Chem. Ind.*, 24, 11.

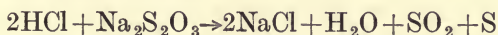
² Guyard, *Zeit. f. anal. Chem.*, 22, 426.

Determination as Oxide

(a) *Precipitation by Ammonium Hydrate.*—The aluminium solution, which should contain several grams of ammonium chloride, is heated to the boiling point in a porcelain or platinum dish for preference. Ammonium hydrate is then added whilst the liquid is being stirred, until there is a slight excess, and the precipitated aluminium hydroxide then allowed to settle. The clear liquid is decanted as far as possible from the precipitate and poured through an ashless filter paper, not through pulp. After washing by decantation several times with hot water containing a small quantity of ammonium nitrate and ammonium hydrate, the precipitate is transferred to the filter, where the washing is continued until the precipitate is free from chlorine. The precipitate should be churned up as much as possible by the hot washing liquid, otherwise unnecessarily large quantities of liquid will be required. The precipitate is ignited to alumina, with or without previous drying, in a platinum crucible.



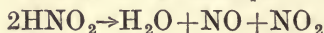
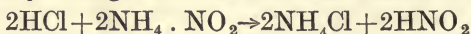
(b) *Precipitation by Sodium Thiosulphate.*—The hydrolysis of aluminium salts in aqueous solution is readily brought about in the presence of sodium thiosulphate, which reacts with the acid formed by the hydrolysis yielding a neutral salt and sulphur.



The aluminium solution, which should have a volume of at least 200 c.c. per decigram of metal present, is made as neutral as possible, and an aqueous solution of 5 to 10 grams of sodium thiosulphate crystals added. The mixture is then boiled until all the sulphur dioxide is expelled, after which a few drops of ammonia are added to produce faint alkalinity and the boiling continued for two or three minutes longer. The precipitated sulphur is thereby balled up, and, by mixing with the precipitated aluminium hydroxide, renders the latter much easier of filtration and washing.

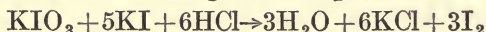
Hot water is used for the latter operation. Ignition leaves a residue of alumina as in the preceding method.

(c) *Precipitation with Ammonium Nitrite*.—Wynkoop¹ and Schirm² suggested the use of ammonium nitrite as the hydrolytic agent, the reactions between it and the mineral acid yielding a neutral salt and oxides of nitrogen.



If the solution is acid, very dilute ammonia, or ammonium carbonate solution, is added a little at a time, with constant stirring or shaking after each addition, until the precipitate which forms at each addition can only just be dissolved. Should a permanent precipitate be inadvertently obtained, it is dissolved in the least possible quantity of dilute acid. The clear solution consists of a very highly basic chloride of aluminium, the proportion of hydroxyl to chlorine being at least eight radicles to one. A large excess of a 6 per cent. aqueous solution of ammonium nitrite is then added, the solution diluted to a large volume and boiled until the nitrous fumes are completely expelled. A few drops of ammonia are then added, the precipitate is allowed to settle, filtered, washed with hot water, and ignited as before to alumina.

(d) *Precipitation with Iodide-iodate Mixture*.—A mixture of potassium iodide and iodate reacts in solution with free hydrochloric acid according to the equation



By means of such a mixture the salts of several metals are capable of hydrolysis, and the determination of aluminium in particular is readily effected by collecting the precipitated hydroxide.

Stock³ recommends that the solution be made slightly acid; if it is too much so, sodium hydrate solution is added until a faint permanent precipitate is obtained, and this is then just redissolved. The iodide-iodate mixture is then added, the liquid stirred and allowed to stand for five

¹ Wynkoop, *Journ. Amer. Chem. Soc.*, 19, 434.

² Schirm, *Chem. Zeit.* (1909), 877.

³ Stock, *Berichte* (1900), 548.

minutes. The liberated iodine is then taken into combination with a 20 per cent. solution of sodium thiosulphate, after which a further small quantity of the reagent is added to make sure of complete precipitation. If any colour results, a drop or two more of the thiosulphate solution is added and the mixture allowed to stand on the water bath for about half an hour. The precipitate of aluminium hydroxide which is thus obtained is capable of comparatively rapid filtration and washing.

The precipitation mixture consists of equal volumes of a saturated solution of potassium iodate (which contains about 7 per cent. of the solid), and a 25 per cent. solution of potassium iodide.

Determination as Phosphate

This excellent method consists in the precipitation of aluminium as orthophosphate, in which form it is also weighed. The solution, containing not more than a decigram of aluminium, is treated with 2 or 3 grams of sodium phosphate or the equivalent of them in the form of a saturated solution. If the solution was originally neutral, the sodium phosphate will produce a precipitate, which should then be taken into solution with hydrochloric acid, of which a further excess of about 1 c.c. is added. If no permanent precipitate is obtained on the addition of the phosphate, ammonium carbonate solution is added until one is obtained, and this is taken into solution again as before. To the liquid, which should occupy a volume of 300 to 400 c.c., from 5 to 10 grams of sodium thiosulphate are added, the liquid brought to the boil, and 20 c.c. of acetic acid added. The boiling is continued for about ten minutes in order to coagulate the precipitated sulphur, the precipitate collected, washed with hot water, dried and ignited along with the filter to AlPO_4 containing 22.19 per cent. of aluminium.

The authors are of opinion that the phosphate method is much better than any one of the modifications of the hydroxide precipitation, being not only accurate, but very

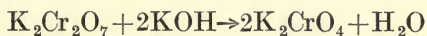
easy of manipulation. The large excess of phosphate introduced appears to be necessary in order to secure the formation of a phosphate of definite composition, experience having shown that whilst smaller quantities may yield a complete removal of the aluminium from the solution, yet the precipitate containing it is of indefinite composition. The method constitutes the best means of separating iron and aluminium. Iron is reduced and retained in the ferrous condition by the sulphur dioxide generated, and ferrous phosphate does not precipitate from solutions containing acetic acid.

Chromium

Although this metal is found in the same analytical group as iron and aluminium, it presents many and important differences from them. If the properties of the three metals are surveyed, it is seen at once that there is a considerable gradation of properties from iron on the one side to chromium on the other. The properties of the oxides demonstrate this as well as those of any other set of compounds. Iron gives two oxides, both (relatively) definitely basic in their properties. Aluminium gives only one oxide which may be considered almost as neutral as it is possible for an oxide to be. In the presence of a strong base the oxide of aluminium acts as an acid, and in the presence of a strong acid it acts as a base—producing in each case a very unstable compound (*cf.* the hydrolysis of aluminium salts). Chromium gives a series of compounds corresponding to three different states of oxidation— CrO , Cr_2O_3 , and CrO_3 . Of these the first oxide has only basic properties, the second has the properties of ferric or aluminic oxide, being equally prone to the production of weakly bound compounds, whilst the third and by far the most important oxide is strongly and definitely acidic in its properties. This oxide, CrO_3 , and its compounds are the most stable and most certain in reaction among the compounds of chromium, and in consequence they are used almost exclusively for the estimation of the metal. Still more important for this purpose is the

fact that the degradation of the compounds of the acid oxide to those of chromic oxide can be made to take place quite quantitatively under many convenient conditions, and as a result permits of the use of standard volumetric processes.

The most important compound of chromium is certainly potassium dichromate ($K_2Cr_2O_7$), which is produced in the wet way from most of the salts of chromic oxide by the action of powerful oxidising agents. This compound is perfectly stable in moderately acid solutions. In alkaline solutions it passes into potassium chromate (K_2CrO_4) according to the reaction



On acidification the dichromate is reformed. (This change does not influence any of the volumetric reactions, as the state of oxidation of the chromium is not altered in any way at all.)

The salts of chromium have no greater stability in solution than those of aluminium, and the methods employed to give the hydrolysis a useful turn in the case of aluminium would apply almost equally in the case of chromium. Of gravimetric methods only one has ever been used to any great extent, and that is the precipitation of the green chromic hydroxide from solution of chromic salts, followed by ignition to the green oxide Cr_2O_3 . The usual method is the ammonia and ammonium chloride precipitation. In filtering, &c., the precipitate does not show any superiority over aluminium hydroxide. It may be improved, however, if the precipitation is made in the presence of hydroxylamine. Like most gelatinous precipitates (which, as a rule, present a very considerable surface area) the tendency to adsorption is very great, and as a result the precipitation of this compound must take place from nearly pure solutions. The phosphate precipitation may be used under almost exactly the same conditions as for aluminium, though the composition of the precipitate does not correspond to $AlPO_4$, being a basic compound $3Cr_2O_3 \cdot 2P_2O_5$. In the presence of sufficient excess of ammonium phosphate and of sodium thiosulphate this composition is reliable. Even if not used

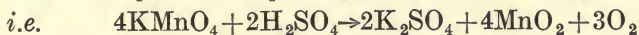
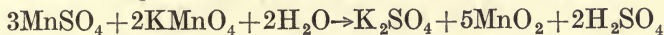
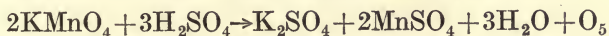
for the actual estimation, this precipitate is useful at times as a means of separating the chromium from an impure solution, as the precipitate of basic phosphate is fairly pure (*i.e.* does not adsorb to any very marked extent). The precipitate is generally redissolved afterwards, and the solution treated by the precipitation of the chromium as oxide, this being the standard form in which the precipitate is weighed.

In addition to these methods, in which the precipitate contains the chromium as base, some methods have been devised in which the chromium is present as a compound of CrO_3 . The chromates of the heavy metals are insoluble in solutions of weak acids (*cf.* the volumetric estimation of lead, p. 58, for conditions). Lead, barium and mercurous salts may be employed, the two first being the more suitable. (If ammonium salts are present, the mercurous salts are impossible.)

The volumetric processes for chromium are the ones in almost universal use. They depend upon the production of the acid compounds from those of chromic oxide, by means of wet reactions. (Occasionally, of course, the employment of dry methods, *e.g.* fusion of chromic oxide with an oxidising and basic mixture, is a necessity.) The most useful reagents for use in the wet are potassium permanganate, and a mixture of nitric acid and potassium chlorate. Many others have been suggested, and some are in use, but the most popular is potassium permanganate. (Another interesting and very satisfactory process is the electrolysis of a solution of chromium chloride containing a little free hydrochloric acid and an excess of ammonium oxalate. The conversion is complete at ordinary temperatures in a few hours—*cf.* analysis of stellite, p. 205.) For the potassium permanganate oxidation the solution should contain about 10 per cent. of sulphuric acid, and should be boiling. The potassium permanganate is added as a strong solution to the boiling liquid, and is added until a permanent brown precipitate or a permanent purple colour is produced. From this stage three processes may be adopted. The essential point is to destroy completely all excess of potas-

sium permanganate that exists in the solution. Unless this is done, there is no chance of the estimation being useful.

(1) The solution may be boiled until the potassium permanganate is broken down, by a process of self-oxidation, to manganese dioxide. The reactions are probably



This reaction takes about ten minutes to accomplish. When it is completed, the solution, which contains potassium dichromate and the precipitated manganese dioxide, is allowed to settle, and then the clear hot liquid is decanted and the precipitate washed by decantation with hot water fairly thoroughly, before being transferred to the filter paper. (In all probability the manganese dioxide which is thrown down in the early stages of the reaction takes a part in completing the oxidation of the chromium sulphate to potassium dichromate. It is possible to perform the whole of the oxidation with manganese dioxide if desired.) The filter used is best if prepared of asbestos pulp, as the cellulose of a filter paper has a distinct reducing action upon the hot potassium dichromate. When cold, the solution is titrated with any suitable reagents—most usually with standard ferrous ammonium sulphate and potassium permanganate.

(2) The destruction of the excess of potassium permanganate is effected much more rapidly if a little manganese sulphate is added to the solution. After allowing the solution to boil for a few minutes, after the addition of the permanganate solution, in order to ensure the oxidation of the chromium sulphate, the solution is treated with a pinch of manganese sulphate (the flask being removed from the hot plate before making the addition). Generally as much of the salt as will cover the end of a spatula is sufficient to complete the action. After boiling for another couple of minutes, the solution is allowed to settle, and is filtered as above. The precipitate obtained in this case is filtered much

more easily than in the first. The titration is done as before.

1 c.c. of $\frac{N}{10}$ $\text{KMnO}_4 = 0.001736$ gram chromium.

(3) A filtration may be avoided entirely if the manganese dioxide can be destroyed in the solution by means of some reagent which will not attack the potassium dichromate. The most useful is hydrochloric acid. The solution in which the precipitation is made should be of considerable bulk (300 to 400 c.c.). When the oxidation is complete (after ten minutes' boiling), add concentrated hydrochloric acid little by little until the precipitate has just disappeared. Then dilute with 150 c.c. of hot water, and boil until all the chlorine has been expelled. This must be accomplished quickly, but completely. If any chlorine is left in the solution during the titration, it will act on the reducing agent used in the titration. Also if there is any concentration of the solution, there is a possibility of reaction between the potassium dichromate and the hydrochloric acid, causing a low result. When all the chlorine is expelled, the solution is cooled and titrated with standard ferrous ammonium sulphate and potassium dichromate (*not* potassium permanganate). The disappearance of the chlorine is detected by the use of an iodide-starch paper.

CHAPTER XII

NICKEL

NICKEL is one of those metals that are not precipitated by ammonia in the presence of any small quantity of ammonium salts, as the latter, together with the nickel, form complex compounds having the nickel either in the negative parts of the compound or else in combination with ammonia as a complex cation which is not decomposable by such a weak base as ammonia. These compounds may be broken down, however, by the caustic alkalies. These produce the green nickelous hydroxide $\text{Ni}(\text{OH})_2$ corresponding to the lowest oxide NiO . This fact is not to be utilised for a gravimetric estimation as the precipitation is not complete, and to produce a suitable precipitate it is better to throw down the higher oxide in its hydrated form by means of a caustic alkali and bromine water (*i.e.* to oxidise the nickel with the alkaline hypobromite, and then precipitate the metal with the excess of alkali). This produces the black nickelic hydroxide, the precipitation being quite complete. The hydroxide may be estimated by direct ignition to Ni_2O_3 or by long ignition to NiO , and weighing as such. In practice this method suffers from the extremely tedious washing that always accompanies precipitations made with the caustic alkalies.

The old standard method for the gravimetric estimation was the estimation as metal—by reduction of the oxides in a stream of hydrogen. The oxides may be replaced by the hydroxides or the carbonates. This method is, of course, quite satisfactory so far as the results are concerned, but is not at all pleasant to perform, being much more tedious in the operation than several other methods which in consequence have displaced it from favour.

The sulphide of nickel is another compound which under certain circumstances may be employed. Nickel sulphide is precipitated in alkaline solutions and in solutions of some very weak acids, but when once it is formed it is not at all soluble in dilute acids. It is very slightly soluble, though quite appreciably, in alkaline sulphides. After filtering the precipitate, the washing must be done by means of water saturated with sulphuretted hydrogen. The ignition of any of these sulphides must be done in a Rose crucible, through which a stream of hydrogen is passed. The precipitate must be mixed with sulphur to prevent the formation of a mixture of sulphate and oxide. Nickel sulphide can also be roasted quantitatively to the oxide NiO . To do this the filter should first be "ashed" into a porcelain crucible, the main precipitate then added, powdered with a rounded glass rod, and heated over a small flame for 15 minutes. The crucible is finally subjected to the full red heat of the muffle for half an hour.

Nickel may be estimated as phosphate on lines similar to those described for cobalt. Of the more recent methods that have been proposed, no others have gained the popularity that is accorded to the precipitation with dimethylglyoxime. This is described in full below. A similar method employs diphenylglyoxime, the object being to increase the weight of the precipitate. Another method of precipitation, on somewhat similar lines, is that which employs dicyandiamidine. This does not appear to have any advantages over the precipitation with dimethylglyoxime, and is hardly, if ever, employed.

Apart from the cyanometric method of estimation, which is described below in full, there are only a few proposals for volumetric methods of estimation. Two of these require the preliminary precipitation of the nickel as hydroxide. The first one throws down the apple-green nickelous hydroxide, which need not be filtered away, but just allowed to react at once with potassium iodide, added after the potash. The precipitate and the potassium iodide interact, producing iodine, which is estimated directly with sodium thiosulphate. The other method recalls the esti-

mation of manganese peroxide in pyrolusite, and similar operations with peroxides. The nickel is precipitated with the oxidising mixture of bromine and potash. The precipitated nickelic hydroxide $\text{Ni}(\text{OH})_3$ is added to a known quantity of ferrous sulphate solution, which is oxidised by the peroxide of nickel, the latter being reduced to its lower oxide and passing into solution as nickel sulphate. By estimating the excess of ferrous sulphate, the quantity oxidised by the nickelic oxide is obtained, and hence the nickel. The only drawback to this method is the fact that the precipitate is of a rather uncertain composition, it being not at all regular at $\text{Ni}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. As the method depends for its usefulness upon the ratio $\text{Ni}/\text{O} = 2/3$, any variations destroy its value.

Parr and Lindgren¹ have proposed a volumetric method to accelerate the one which uses the precipitation with dimethylglyoxime. They dissolve up the precipitate of dimethyl nickel glyoxime in standard sulphuric acid, and then titrate the excess of acid with standard potash solution. The end point is marked, without the addition of other indicator, by the appearance of a faint yellowish colour.

Undoubtedly after copper, nickel is the element most frequently estimated electrolytically. In general practice only two methods are ever employed. The first, and perhaps the most widely used, is that of the deposition from a double salt of nickel and ammonium in a solution containing a large excess of ammonia. In practice this method is carried out in a solution containing some 30 per cent. of free ammonia. This may be submitted to currents of most ordinary strengths depending upon the time that is available, and is quite well suited to rotatory depositions. The E.M.F. for stationary depositions should be from three to four volts and the current density about 1.0 to 1.5. As a rule the sulphate is the salt employed, and the various details can be obtained from the papers of Gooch and Medway,²

¹ Parr and Lindgren, *Trans. Amer. Brass Founders' Ass.* (1911), 5, 120.

² Gooch and Medway, *Amer. Journ. Sci.* [4], 15, 320.

Exner,¹ Fischer,² E. F. Smith and Kollock,³ and E. F. Smith,⁴ but it has been shown by Thiel⁵ and by Windelschmidt⁶ that it is possible to use the nitrates if precautions are taken to remove the nitrous acid that may be formed in the solution during the various operations. Oettel⁷ has shown, too, that the chlorides may be employed. His solution contains about 10 grams of ammonium chloride to 1 gram of nickel as chloride, and has the usual quantity of free ammonia. The current density that he employs is 0.4.

All the other methods may be said to be included in this one class as they all employ a solution of the double salt of nickel and ammonia with an organic acid, in an ammoniacal solution. Of these by far the most common is that of the double oxalate, a method first proposed by Classen and v. Reis.⁸ In this method the nickel salt is associated with at least six times its weight of ammonium oxalate, and the electrolyte contains a small quantity of free ammonia. (This solution is a rather unfortunate one for the precipitation on a dish cathode. The solubility of ammonium oxalate in water—particularly if it contains free ammonia and other salts—is by no means so high that the preparation of a solution containing 6 grams of ammonium oxalate in 150 c.c. is an easy matter.) With such a solution the current density is about 1.0 and the E.M.F. about 4.5 volts. Besides the oxalate solutions, the deposition may be performed effectually in either tartrate, citrate, or acetate solutions as recommended by various writers (Wrightson,⁹ Ohl,¹⁰ Schweder,¹¹ Smith and Muhr¹²). Of these solutions the tartrate gives the most satisfactory results. The nickel

¹ Exner, *Journ. Amer. Chem. Soc.*, 25, 896.

² Fischer, *Zeit. Elektrochem.*, 13, 469.

³ E. F. Smith and Kollock, *Journ. Amer. Chem. Soc.*, 27, 1255.

⁴ E. F. Smith, *ib.*, 26, 1595.

⁵ Thiel, *Zeit. Elektrochem.*, 14, 201.

⁶ Windelschmidt, *Dissertation*. Münster, 1907.

⁷ Oettel, *Zeit. Elektrochem.*, 1, 194.

⁸ Classen and v. Reis, *Berichte*, 14, 1472.

⁹ Wrightson, *Zeit. anal. Chem.*, 15, 300.

¹⁰ Ohl, *ib.*, 18, 52.

¹¹ Schweder, *ib.*, 16, 344.

¹² Smith and Muhr, *Journ. App. Chem.*, 5, 488, and 7, 189.

salt is mixed with about three times its weight of ammonium tartrate and electrolysed with a low current density—about 0.6. (The best results are obtained with current density 0.1 to 0.2 during a protracted electrolysis.) The E.M.F. is about 4.5 volts. All these organic salts are liable to produce deposits which are contaminated with small specks of carbon. This is generally more noticeable with the deposits from high current densities. A solution containing sodium phosphate and free phosphoric acid has been recommended, but is stated by Perkin to give low results. Another suggestion which is stated to work satisfactorily, is that of Nicholson and Avery¹—the addition of sodium borate to the solution of sodium oxalate and nickel. Perkin prefers to use an ammoniacal solution of ammonium borate and to electrolyse this with a low current density.

Gravimetric Determination with Dimethylglyoxime

Before the appearance of this method, which was outlined first by Tschugaeff² in 1905, there was no suitable and reliable method for the gravimetric estimation of nickel. Besides being a very admirable method of precipitation, this process also provides a suitable method for the separation of nickel from almost any other metal. It certainly provides a perfect separation from iron and cobalt, from copper (after two precipitations), from tin, lead, &c. The precipitation has been improved by Krant,³ and Brunck,⁴ whilst its application to German silver has been perfected by Spring⁵ and Ibbotson.⁶ Under these workers the precipitation has assumed the following form. The nickel may be present in the form of almost any of its soluble salts, but should not be associated with any metals that are precipitated by ammonia (unless they can be prevented by the addition of

¹ Nicholson and Avery, *Journ. Amer. Chem. Soc.*, 18, 654.

² Tschugaeff, *Zeit. anorg. Chem.*, 46, 144, or *Berichte*, 38, 2520.

³ Krant, *Zeit. angew. Chem.*, 19, 1793.

⁴ Brunck, *ib.*, 20, 834.

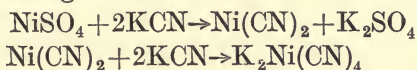
⁵ Spring, *Chem. News*, vol. 104, p. 58.

⁶ Ibbotson, *Chem. News*, vol. 104, p. 224.

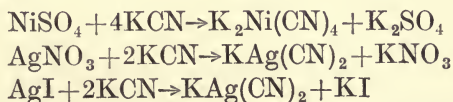
tartaric or some similar acid). The ammonia is added to the solution in slight excess—not a great excess, or otherwise there is a hindering of the precipitation. When distinctly alkaline, heat the solution to about 50° C.—not more—and add sufficient of the reagent to precipitate the whole of the nickel. The reagent is a white crystalline powder, and is prepared as a 1 per cent. solution in alcohol (or spir. vin. rect. if preferred). The precipitate comes down as a bright red flocculent mass which does not settle at all rapidly. The solution and precipitate should be maintained at 50° C. for about a quarter of an hour, and then filtered. This may be done either on to paper pulp or on to a Gooch crucible. In either case the precipitate shrinks very rapidly on the filter, and is handled with a much greater ease than might be expected from its first appearance. It may be washed quite easily, but this should be done with a dilute solution of ammonium nitrate, in which the precipitate is not soluble, though it is to a small extent in water. If the dimethyl nickel glyoxime is collected on a Gooch crucible, the precipitate is best dried gently in an air bath at about 120° C. and weighed as $\text{NiC}_8\text{H}_{14}\text{N}_4\text{O}_4$, containing 20.32 per cent. of nickel. Overheating is to be avoided so far as possible, as the precipitate is volatile completely at 250° C.—subliming without decomposition. By taking sufficient precautions it is possible to ignite the precipitate to nickel oxide, an operation very much to be preferred if any large number of estimations are to be made. To effect this change, great care must be taken to prevent any volatilisation. The easiest way (and one which works admirably) is to take the paper pulp after sucking dry at the pump, and to place it in a porcelain crucible wrapped up in two *damp* filter papers. These are not allowed to dry before being placed at the mouth of the muffle, where they may be charred quickly. After the charring is complete, the crucible and its contents are placed further in the muffle, and the ignition proceeded with at once. Under these conditions there is no loss of nickel, the whole remaining in the crucible as green nickel oxide (NiO), in which form it may be weighed.

Volumetric Determination

Most of the common metals, particularly those met with in commerce, react with potassium cyanide, giving first a precipitate, and then by the addition of more potassium cyanide, forming a soluble double cyanide. These double cyanides that result may be divided into two classes, according to whether they are stable in the presence of dilute acids or are decomposed by them. The double cyanide of nickel and potassium belongs to this latter class, those of iron and cobalt to the former. In the case of a good many of these metals (including nickel), the reaction between the metallic salt and the potassium cyanide is perfectly quantitative, and by taking note of the total disappearance of the last particles of the precipitated metallic cyanide, an accurate measure of the quantities of the metal present may be made according to the reactions



If the precipitated nickel cyanide be taken as its own indicator, the result is not particularly satisfactory, because the end point is not distinct enough. If, however, some other substance can be found, which in the solution will act in the same way and at the same time is more conspicuous, by adding suitable quantities of this compound an easy estimation is produced. Such a substance is found in silver iodide. This is produced by the addition of a few crystals of potassium iodide to the solution before the titration is commenced, and then adding a little silver nitrate before adding any of the potassium cyanide at all. The result is that there is present in the solution silver nitrate, nickel sulphate (*e.g.*) and a precipitate of silver iodide. On adding the potassium cyanide, the reactions take place in the following order :



Evidently, then, the whole of the indicator turbidity is re-

moved only when the whole of the nickel has been titrated. The titration must be performed in an alkaline solution, usually ammoniacal, as this prevents the volatilisation of the hydrogen cyanide produced by the hydrolysis of the potassium cyanide, and to a certain extent prevents the hydrolysis. Any considerable excess must be avoided, as a large quantity in the solution has a solvent effect upon the silver iodide and tends to obscure the end point. To sharpen this last some ammonium salt may be added with advantage, and of these the sulphate is by far the best.

First of all, neutralise the cold solution containing the nickel and, after adding 2 c.c. of concentrated sulphuric acid, add ammonia until the solution smells fairly strongly. Add three or four small crystals of potassium iodide, and allow them to dissolve. From a burette add several c.c. of a standard solution of silver nitrate, and then from a second burette add some approximately standard potassium cyanide solution until the turbidity is just discharged. The potassium cyanide solution should be added in a rapid stream of drops, as otherwise there is a formation of crystalline potassium nickel cyanide, which may enclose some nickel and so prevent the complete reaction from taking place. In practice it is found usually to be more convenient to add an excess of potassium cyanide, and then titrate back again with the silver nitrate, it being more difficult to determine the disappearance of a turbidity than its reappearance. Obviously the end point may be produced and destroyed any number of times. Having obtained the end point, add about 20 c.c. of the potassium cyanide solution and again finish with the silver nitrate, to obtain the value of the approximately standard potassium cyanide in terms of the really standard silver nitrate. This standardisation must be performed for each series of determinations, as the potassium cyanide solutions change strength too rapidly to allow of a constant standardisation factor being accepted. The silver nitrate will keep indefinitely. From the standardisation figures obtain the equivalent in silver nitrate of the potassium cyanide used in the titration. From the equations given above it will be seen that as regards potassium

cyanide two atoms of silver are equivalent to one atom of nickel, *i.e.* 216 grams of silver require as much potassium cyanide as do 58.6 grams of nickel. From this relationship the nickel contents of the solution may be obtained.

Electrolytic Determination

(a) If the solution does not contain the nickel in the form of sulphate, add 3 c.c. of concentrated sulphuric acid to it and evaporate to fumes. Cool and dilute the solution to 50 c.c., and boil until everything has gone into solution. Add to the liquid 8 grams of ammonium sulphate, and when this has dissolved transfer the liquid to the electrolytic dish, which has been weighed previously, and make up to the mark with 50 per cent. ammonia. Electrolyse with a current density of about 1.0 and an E.M.F. of about 4 volts. The electrolyte may be warmed with advantage; if this is done the liquid that is supplied to make up for that lost by evaporation must be about 50 per cent. ammonia solution. The electrolysis takes about three and a half hours for 200 milligrams of nickel. To test for the end of the action, take out about half a c.c. and add to it ammonium sulphide solution (colourless). The absence of any brown precipitate or any brown colouration indicates freedom from nickel. The deposit should be washed with water and absolute alcohol, dried, and weighed at once. No time should be allowed to elapse before the deposit is dissolved away from the dish, nitric acid (sp. gr. 1.20) being a suitable solvent.

(b) The solution should not contain much free acid, and should be neutralised. Place it in a beaker, and then add to the solution about 8 grams of ammonium oxalate. When this has dissolved, make ammoniacal, and deposit on the gauze. This should be rotated at about five hundred revolutions per minute. If the solution deposits any of the ammonium oxalate during the deposition, take it all back again into solution by warming the beaker and its contents (surround the beaker by a jar of hot water). Test for the end point as above, and treat the electrode in a similar manner.

CHAPTER XIII

COBALT

COBALT, like nickel, is not precipitated from its solutions by ammonia, the basic compound which forms momentarily being readily soluble in excess of ammonia. The metal, in fact, like platinum and a few others, forms a number of compounds with ammonia, many of them of very complex constitution; they are the cobaltamines. The ammonio-cobaltous compounds readily take up oxygen and form more complex and more numerous ammonio-cobaltic salts, the nickel analogues of which do not exist.

The hydroxides of cobalt must therefore be obtained by precipitation with caustic alkalies, the lower one by using potash alone and the higher one by means of bromine and potash. As in the case of nickel, the oxide resulting from the ignition of the former precipitate (even after prolonged washing) is never potassium-free, and it generally contains silica also. The higher hydroxide can be washed much more effectively and quickly, but the ignited residue in this case also is never silica-free. As, moreover, there seems to be some uncertainty in both cases respecting the composition of the ignited precipitate, which is variously described as CoO , Co_3O_4 , or mixtures of the two, the reduction to metal in a current of hydrogen becomes necessary in this form of determination. Whilst, therefore, the results are generally reliable, they are only obtained at the expenditure of too much time.

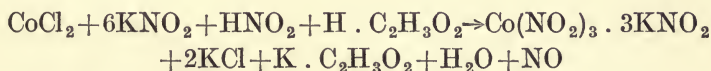
Cobalt, like nickel, is completely precipitated by hydrogen sulphide from solutions made slightly acid with acetic acid, and containing a relatively large proportion of sodium or ammonium acetate. The solution should be heated to incipient boiling before passing the gas. When small

quantities of cobalt are being determined, this form of determination is one of the best, and is described below.

The determination of cobalt as sulphate, which is one of the oldest methods, consists in the evaporation of the solution with a slight excess of sulphuric acid in a capacious crucible. The complete expulsion of the excess of sulphuric acid is marked by a slight darkening in colour round the circumference of the surface of the anhydrous sulphate, and this is taken as determining the end of the ignition. The results are manifestly too high if all free sulphuric acid is not expelled, whereas if heated too strongly the cobalt sulphate begins to decompose, and low results are obtained. The actual temperature interval between complete expulsion of sulphur trioxide and decomposition of cobalt sulphate is not large enough to commend the method for general use.

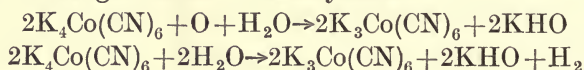
Perhaps the best gravimetric method for the determination of cobalt is the precipitation as its double phosphate with ammonium, whether the precipitate be weighed in that form or ignited to pyrophosphate. Details are given below.

When neutral solutions of nickel and cobalt are treated with a solution of potassium nitrite, double salts of the constitution, $\text{Ni}(\text{NO}_2)_2 \cdot 4\text{KNO}_2$ and $\text{Co}(\text{NO}_2)_2 \cdot 2\text{KNO}_2$ respectively, are formed; these are salts of the lower oxides. The nickel compound is freely soluble. When the solutions are acidified, and preferably with acetic acid, nickel gives the same result, but cobalt forms a sparingly soluble yellow crystalline compound $\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$, in which the metal is in its -ic condition. [This reaction, prior to the introduction of dimethylglyoxime and nitroso- β -naphthol to the analytical chemistry of nickel and cobalt, constituted the best means of separating these two metals.] The change from the -ous to the -ic condition, which may be expressed thus,



recalls the ready oxidation of the ammonio-cobaltous compounds already referred to. The same phenomenon is

encountered with the double cyanide ; a solution of potassium cobalto-cyanide, *e.g.* when boiled with or without access of air, is changed to the cobalticyanide



Nickel does not exhibit this behaviour in any one of the three cases mentioned, nor in the well-known nitroso- β -naphthol reaction, by means of which cobalt and nickel are separated.

Ilinsky and Knorre¹ showed that cobalt can be determined by precipitation with nitroso- β -naphthol. The red precipitate obtained is a cobaltic compound $[\text{C}_{10}\text{H}_6\text{O}(\text{NO})]_3\text{Co}$, and is stable towards dilute hydrochloric acid, whereas the nickel compound which is freely soluble in the same acid is -ous in constitution $[\text{C}_{10}\text{H}_6\text{O}(\text{NO})]_2\text{Ni}$.

Not one of the volumetric methods that have been proposed for the determination of cobalt can be regarded as entirely satisfactory. Iodimetric methods based upon a reduction of precipitated cobaltic hydroxide are rendered uncertain by the indefinite composition of the hydroxide, as is also Winkler's method (and its modifications), which is based upon the oxidation of cobaltous salts by potassium permanganate in the presence of precipitated mercuric oxide.

The cyanometric determination of cobalt is still largely practised, and is carried out in the same manner as the corresponding nickel determination with the silver iodide indicator. If a standard solution of potassium cyanide be run into a suitably adjusted cobalt solution (see Nickel for details), until the silver iodide turbidity is just discharged, it will be found that the amount of cobalt calculated on the basis of the reactions which apply in the case of nickel is not the same as the actual amount present, though it is customary to assume that such is the case. Moreover, the turbidity very quickly reappears, and, if discharged again with a few drops more of cyanide, will again reappear on standing, and so on—so that the difference between the

¹ Ilinsky and Knorre, *Berichte*, 18, 699.

burette reading when the turbidity is first discharged and the reading when a solution is obtained, which remains perfectly clear for, say, five minutes, is considerable. This uncertainty as to the end point, and the fact that the actual amount of cobalt present is not calculable from the cyanide readings, are sufficient to condemn the method. Nevertheless, its rapidity has determined its retention in actual works' practice, a standard solution of known cobalt contents being titrated along with each batch of samples.

The electrolytic determination of cobalt proceeds along exactly the same lines as that of nickel, the conditions which obtain in the deposition from strongly ammoniacal solutions of the sulphate or from the double oxalate solutions being the same in both cases. The lustrous grey deposit (with an entire absence of black specks), which betokens a satisfactory determination, is not obtained so frequently from cobalt as from nickel solutions.

Gravimetric Determination

The particular method to be used for the determination of cobalt depends upon the amount of metal present. For small quantities the precipitation with nitroso- β -naphthol is particularly suitable; as this reagent may not always be available, precipitation with hydrogen sulphide followed by ignition to oxide is recommended. The phosphate method is best adapted to all other cases.

(A) *Precipitation as Sulphide and ignition to Oxide.*—The solution is made feebly acid with acetic acid, and several grams of ammonium acetate added. After heating to boiling, a brisk current of hydrogen sulphide is passed through the solution for about 20 minutes, or until the solution is cold. When only very small quantities of cobalt are present, the sulphide does not begin to precipitate until the gas has been passed for a minute or two, but the precipitation is in all cases complete, given sufficient time. The black sulphide settles very quickly, leaving a clear and colourless supernatant liquid. Without allowing to stand

for any length of time,¹ the precipitate is filtered, washed with hydrogen sulphide water containing a small quantity of ammonium acetate, and dried. The filter and precipitate are then ignited together for about 15 minutes over a small flame in a weighed crucible, the mass finely pulverised, and the ignition continued for half an hour longer in a muffle furnace. If the temperature does not exceed 900° C., and the amount of cobalt sulphide does not exceed about 50 milligrams, the final product has the composition Co_3O_4 , or approximates sufficiently closely to it for all purposes.

(B) *Precipitation as Cobalt Ammonium Phosphate*.—The precipitation of zinc as zinc ammonium phosphate has been shown by Dakin² to be applicable to manganese and cobalt. The authors have used the method very largely for the determination of cobalt, and are able to testify to its accuracy.

The solution is adjusted to the faintest acidity, as in the case of zinc, heated nearly to boiling, and a solution of ammonium phosphate or microcosmic salt (the latter preferred), containing from ten to twenty times the amount of cobalt present, added whilst the liquid is stirred vigorously. The addition of ammonium chloride is unnecessary. The bulky flocculent violet cobalt phosphate (probably an orthophosphate), which forms at first, slowly changes on digestion, with occasional stirring, to a beautiful red crystalline precipitate. The change is accompanied by much shrinkage in volume and corresponding increase in density. When the change is complete, the precipitate is collected in a Gooch crucible if it is desired to weigh it as such, or on ashless paper pulp if it is to be ignited to pyrophosphate. In either case the mother liquor is used for detaching any particles adhering to the sides of the beaker; these are sometimes difficult to remove, particularly if the rod has come into contact with the sides of the beaker during the stirring operation. The final washing is done with water. When dried at 100° to 105° C. the precipitate has the composition

¹ Cobalt sulphide precipitated in this manner slowly dissolves again on standing. A precipitate inadvertently left to stand for several weeks passed almost completely into solution again.

² Dakin, *Zeit. f. anal. Chem.*, 39, 784.

$\text{CoNH}_4\text{PO}_4 + \text{H}_2\text{O}$. If ignited to pyrophosphate, great care is necessary at the beginning of the operation to prevent loss by projection from the crucible along with the escaping ammonia and water vapour resulting from the decomposition.

(C) *Precipitation with Nitroso- β -naphthol*.—This method is extremely valuable for the determination of small amounts of cobalt, and for the separation of such from comparatively large amounts of nickel. The solution, containing about 5 c.c. of hydrochloric acid, is warmed and the nitroso- β -naphthol reagent added hot until no further precipitate appears to be formed. The precipitate is red and very voluminous. It is allowed to settle and the supernatant liquid tested to ascertain the completeness of the precipitation. Several hours at the ordinary temperature are allowed for settling before filtration is proceeded with. The precipitate is washed first with cold water, and then, in the case of separations from nickel, with hot 12 per cent. hydrochloric acid until the nickel is removed, and lastly, with hot water until free from acid. The dried precipitate is ignited in a Rose crucible, very carefully at first, the temperature being raised finally to that of full redness. The complete removal of carbon is facilitated by the previous addition of a small quantity of oxalic acid. The oxide is finally reduced to metal, in which form it is weighed.

The nitroso- β -naphthol should be freshly prepared for each precipitation or at frequent intervals, as the solution does not keep very well. It is made by dissolving the solid in glacial acetic acid at the rate of 2 grams to 75 c.c. of acid; the solution so obtained is diluted with its own volume of water, and filtered for use.

Volumetric and Electrolytic Determinations.—These are dealt with at sufficient length in the foregoing introduction.

Separation of Cobalt from Nickel

The two methods almost exclusively practised at the present time for the separation of nickel and cobalt have already been described. The dimethylglyoxime method

is applicable to almost all cases, but is not so good as the nitroso- β -naphthol precipitation for small quantities of cobalt in the presence of large amounts of nickel. The older method of precipitation of the cobalt as the double nitrite of potassium and cobalt has passed out of general use, but another old one in Liebig's ¹ potassium cyanide method is still of sufficient importance to deserve description.

The solution is adjusted to neutrality, a large excess of pure potassium cyanide added, and then several grams (about five) of pure potassium hydroxide. Bromine water is next added, with constant stirring until no further precipitation takes place. The precipitate is the black nickelic hydroxide. The success of the method depends upon the maintenance throughout of strong alkalinity in the solution. After dilution, the nickelic oxide is collected and determined as usual. The cobalt remains in the filtrate as potassium cobalticyanide. When a determination of the cobalt is required, the filtrate is acidified with sulphuric acid, evaporated to low bulk, several more c.c. concentrated sulphuric acid added, and the mixture fumed strongly. After cooling and diluting with water, the cobalt exists as sulphate, along with sulphates of potassium and ammonium, and is determined gravimetrically or electrolytically.

Liebig, *Ann. d. Chem. u. Pharm.*, 65, 244 ; 87, 128.

CHAPTER XIV

ZINC

THE compound employed most frequently for the gravimetric determination of zinc used to be the sulphide. Unfortunately zinc sulphide has many undesirable properties, particularly connected with filtering and the allied operations of washing. These properties render it just as unsuitable for the gravimetric as for the volumetric estimations to which it is essential, and which are discussed below. The gravimetric methods either precipitate the sulphide from an ammoniacal solution or from one in which the acidity has been reduced to the absolute minimum. After precipitation the sulphide is filtered out and washed as clean as possible, then either roasted in a Rose crucible with sulphur or else ignited gently to the oxide. The actual precipitation is accomplished by the use of various reagents—either hydrogen sulphide or ammonium or sodium sulphide or by boiling the solution with flowers of sulphur. The other old-established methods rely upon the precipitation by a soluble carbonate and the boiling of the precipitate to hydroxide followed by ignition to oxide. Both of these types of estimation are needlessly long and clumsy, and in all probability seldom used now, the only gravimetric method which can be said to claim any wide recognition being the precipitation of the double phosphate of zinc and ammonium.

Bertrand and Javillier¹ have described an interesting method for the determination of small quantities of zinc. They prepare a solution containing 10 to 15 per cent. of concentrated ammonia, and precipitate the zinc as calcium zincate and carbonate by the addition of 50 c.c. of a saturated solution of lime. From the resulting precipitate the

¹ *Comptes Rend.* (1906), 143, 900–942.

calcium is removed by precipitation as oxalate after redissolving. Apart from these three methods, zinc does not appear to be estimated gravimetrically.

Zinc is one of the most strongly electro-positive of those metals occurring in commerce, and in consequence it is difficult, though not impossible, to deposit the metal from solutions containing hydrogen ions. The most usual method is to employ alkaline solutions, taking advantage of the fact that zinc will form zincates with the alkali metals. These may be electrolysed on the same lines as are employed for double cyanides, oxalates, &c. Despite the fact that if the hydrogen ions are present in any sufficient quantity they will be deposited in preference to the metal, their number may be reduced to such a point that the deposition of the zinc requires less work to be performed than does the liberation of the hydrogen. Under these circumstances the metal is deposited quite satisfactorily. Such acid solutions as are employed must be necessarily those containing acids of low dissociation constant, and the concentration of the hydrogen ions is reduced still further by the addition of an almost completely ionised compound containing an ion in common with the acid. Most usually one of the neutral salts of the acid and the alkali metals is employed. One particularly favourite mixture is that of acetic acid and sodium acetate, though perhaps even more used is that of ammonium oxalate and oxalic acid. (In this latter case the reagent produces a precipitate of zinc oxalate, which is redissolved by excess of the reagent and gives a solution of zinc ammonium oxalate which has for ions NH_4^+ and $(\text{Zn}(\text{CO}_2)_4)^{2-}$.)

For the alkaline deposition the proportion of alkali to zinc is not of great importance provided that it exceeds a minimum of ten molecules of alkali to one molecule of zinc salt.¹ There is no point in the employment of any larger excess of the alkali than is required to keep the solution clear. This solution is suited to either stationary or rotatory deposition, and may be performed to the greatest advantage

¹ Spitzer, *Zeit. Elektrochem.*, 11, 391 (1905).

in the cold. A suitable current is that of density 0.8 and E.M.F. of about 4.0 volts. Spear and Strahan¹ have shown that the most satisfactory results are obtained only if the solution is electrolysed hot at first and cold later. They state that nitrates and ammonium salts must be absent, and prefer to arrange that there shall not be any excess of sulphuric acid before adding the alkali, as the double sulphate of potassium and zinc that is produced is rather insoluble in strong alkalies. Ingham² uses a solution containing an excess of ammonia and some ammonium chloride, and prefers a current density of 5, with E.M.F. of 5 volts. The solution is rotated rapidly. (It is stated that the chlorine liberated at the platinum anode has no ill effects.) Paweck³ employs a solution containing one part of zinc sulphate, twenty parts of Rochelle salt, and twelve parts of strong alkali (usually caustic soda). Hollard's⁴ solution contains an excess of sodium hydrate, to which he adds about 10 per cent. or less of potassium cyanide.

The small quantity of free acid that is permissible in the deposition of the zinc is seen in the instructions given by the various workers (*cf.* Nissenson⁵ and Spitzer⁶). The latter worker uses 5 grams of sodium acetate with less than half a c.c. of glacial acetic acid. This reduces the degree of dissociation if the acid from about 0.04 to about 0.0024. His current density is 0.5. Sand⁷ has shown that in these cases the temperature must be brought down below 30° C. if the deposition is to be complete. In the case of oxalic acid solutions 4 grams of ammonium oxalate are added to the zinc, and then the acid—either oxalic, tartaric, or formic—is added a little at a time. The current density is 0.5 to 1.0 and the E.M.F. 4.2 volts. That the deposition is possible in solutions containing a mineral acid in small quantities, if accompanied by its own neutral salt, is seen in

¹ Spear and Strahan, *Journ. In. Eng. Chem.*, 4, 889 (1912).

² Ingham, *Journ. Amer. Chem. Soc.*, 26, 1280.

³ *Zeit. f. Elektrochem.*, 5 [18], 221–224.

⁴ *Bull. Soc. Chim.*, 29 [7], 266–269.

⁵ Nissenson, *Die Bestimmungsmethoden des Zinks*. Stuttgart, 1907.

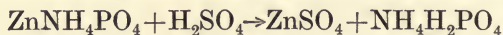
⁶ Spitzer, *Zeit. Elektrochem.*, 11, 404.

⁷ *Trans. Chem. Soc.*, 91, 380.

the instructions of Paweck.¹ He employs a solution of one part of zinc, sixty parts of potassium sulphate or sodium sulphate, and about one part of sulphuric acid.

Probably zinc is the worst metal of all to remove from platinum electrodes, and to avoid the certainty of spoiling the electrodes it is necessary to deposit a thin layer of either copper or silver on the platinum before commencing the estimation. If this precaution is taken, the whole deposit may be removed quite easily by dilute nitric acid. If it is neglected, there is almost a certainty that the platinum will be covered in patches with a black deposit which defies all the efforts of the manipulator to remove it.

Zinc does not afford many possibilities in the way of volumetric estimations. Several have been proposed, but only a very few of them can be said to possess any real value. Probably the best and the most convenient is the titration with potassium ferrocyanide described below, where the limitations of the method are discussed also. Many workers have tried to produce some satisfactory volumetric method through the sulphide. As mentioned above, this compound has one or two unfortunate properties which militate against its usefulness for most analytical purposes. One method is not affected by these properties—a direct titration with sodium sulphide. The end point of the titration is determined by the dropping of a spot of the solution on to a bright silver coin, when a slight excess of the sulphide produces the usual black stain. The precipitated zinc sulphide has no effect upon the silver. This method requires an empirical standardisation of the solution of sodium sulphide for every set of titrations. This fact, taken in conjunction with the rather undesirable character of the reagent, hardly recommends the method. The other methods depending upon the sulphide are iodimetric, and of these the best are described below in full. Another method is connected with the double phosphate precipitation. If the compound is mixed with an acid, it reacts according to



¹ Paweck, *loc. cit.*

By employing an acidimetry indicator to determine the end point of the titration, it is stated that quantitative results can be obtained. The nature of the phosphoric acid makes phenol phthalein a possible indicator in a direct titration, but its use is not to be recommended, for more satisfactory results are obtainable by adding excess of acid and returning with the standard alkali, employing methyl-orange as indicator. Even under the most satisfactory conditions, the method is not to be recommended.

For zinc dust a neat method is that of adding the dust to an acid solution containing ferric sulphate, allowing the zinc to dissolve completely, and then titrating the resulting ferrous sulphate. Another method is to add the zinc dust to Fehling's solution, and when the action is finished titrate the unchanged copper with a standard solution of glucose.

Gravimetric Determination as Phosphate

Of all the gravimetric estimations that have been proposed, the only one that can be recommended without reserve is the precipitation as the double phosphate of zinc and ammonium. The phosphates of those metals that are met with in most alloys fall into three classes. The first includes those insoluble in water and insoluble in weak acids, the phosphates of the sesquioxide metals being members of this group. The phosphates of the divalent metals of Group III B (nickel group) and of Group II are insoluble in water, but soluble in weak acids. Zinc falls in this latter class. The third class contains those phosphates that are soluble in water. The limitations of the method thus will be sufficiently plain to need no further reference. The solution of the zinc must be neutralised very carefully, and, after bringing to the nearest to neutral that is possible, should be made *very faintly* acid with a drop or two of hydrochloric acid. Then about 10 grams of ammonium chloride should be added to the solution, which is brought to an incipient boil. This is followed by the addition of a solution of ammonium phosphate sufficient to precipitate about

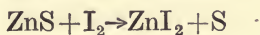
twenty times the weight of zinc that is present in the solution. At first the precipitate is very flocculent, being the normal zinc phosphate, but after standing for a little time at a temperature near the boiling point, the flocculent precipitate changes to a very definitely crystalline form—being the double phosphate of zinc and ammonium $\text{Zn} \cdot \text{NH}_4 \cdot \text{PO}_4$. This settles well in the vessel, and clings very tenaciously to the glass. When all the precipitate appears to be in this crystalline form, filter it on to pulp and clean the beaker very carefully, using a policeman and some of the mother liquor that has already passed through the filter. Finally, wash with water, remove the precipitate to a *porcelain* crucible, and ignite gently at the mouth of the muffle. The temperature must not be very high, and occasionally a little of the filter paper becomes charred and incorporated with the precipitate. If this happens, the burning out of the paper will be tedious unless the precipitate is crushed to a powder with a glass rod. This operation also assists the change from the double phosphate which is precipitated, to zinc pyrophosphate, $\text{Zn}_2\text{P}_2\text{O}_7$, which contains 42.88 per cent. of zinc.

Volumetric Determination

(A) *Iodimetric*.—This method takes advantage of the perfectly quantitative reaction between hydrogen sulphide and iodine. In alkaline solutions zinc may be precipitated perfectly quantitatively as zinc sulphide, but not as a rule in acid solutions. If, however, a weak acid is used, and its “strength” decreased again considerably by the addition of a quantity of one of its own neutral salts, it is possible to produce a perfect precipitation of the zinc sulphide. Such a solution (possessing the necessarily low concentration of hydrogen ions, to allow of the requisite high one of sulphide ions) is one of 5 per cent. formic acid and 1 per cent. of sodium formate.¹ This solution possesses two very great advantages.

¹ Funk, *Zeit. anal. Chem.*, 1907 [47], 93–106, and Doehler, *Chem. Zeit.*, 1899 [37], 399.

Firstly, the zinc is precipitated in a form which may be filtered. This is much more than can be said of the precipitate from ammoniacal solutions. This one particular advantage of the acid precipitation over the alkaline is quite sufficient to compensate for the slightly increased trouble in the preparation of the solution. Even if the precipitate of the sulphide from the ammoniacal solutions is assisted by the co-precipitation of barium sulphate, or by any of the other aids that have been proposed, it is very difficult to handle. Secondly, the precipitation of the zinc may be performed in solutions containing as much as twice its weight of nickel or more than twice its weight of manganese, an equal weight of iron or one-fifth of its weight of cobalt, without any contamination. This is of particular advantage in the analysis of German silver. Thirdly, the precipitation of the zinc sulphide may be performed in solutions containing ordinary quantities of ammonium thiocyanate. This reagent is present in general as excess after the separation of copper in brasses and bronzes which have not been treated electrolytically, and the advantages of a volumetric method which works quite satisfactorily in the presence of this substance are manifest. When the zinc sulphide is produced and filtered, the sulphur may be determined by either titrating the precipitate directly with the iodine,



or the sulphur may be liberated as sulphuretted hydrogen by the addition of acid, and this gas titrated directly.² This latter procedure is to be preferred very much, the end point being quite sharp and clear. The actual method is as follows:—Prepare the solution (which should be free from nitric acid) to exact neutrality, and then add formic acid so that the solution contains not more than 4 per cent. A suitable concentration is 5 c.c. of acid in 150 c.c. of solution. To this mixture add 1 gram of either sodium or potassium formate. Pass a stream of sulphuretted hydrogen for from ten to twenty minutes, depending upon the quantity of zinc

¹ Knaps, *Chem. Zeit.*, 1901, 25 [51], 539–540.

² Müller, *Bull. Soc. Chem.*, 1907 [4], 1, 13–16.

that is present. Remove as much of the excess of hydrogen sulphide as possible from the solution by passing in a stream of carbon dioxide. Filter the precipitate on a tightly packed pulp filter, using a suction pump. Thoroughly wash the precipitate and the pulp with a dilute solution of ammonium chloride or sulphate, suck dry and transfer the precipitate and paper entirely to a beaker, and add 150 c.c. of water. Add a little starch solution, and then acidify the mixture. At once titrate with iodine of a suitable strength. One gram of iodine is equivalent to 0.248 gram of zinc. Pouget¹ recommends the addition of a fairly large excess of iodine solution, and a retitration with standard sodium thiosulphate. His work was done on the precipitated zinc sulphide rather than the sulphuretted hydrogen, and in that case his recommendations may be followed with advantage, for the reaction between the sulphide and the iodine is somewhat slow. If allowed to stand along with the excess, the reaction may be allowed to go to completion, and then titrated back again at leisure. In the case of the liberated sulphuretted hydrogen there is no necessity for such a procedure. Knaps² proceeds likewise in the formation of the zinc sulphide, but adds 10 to 20 c.c. of a solution of barium chloride containing 150 grams per litre, and an equal volume of a solution of sodium sulphate containing 200 grams per litre. This produces a precipitate which under ordinary circumstances it is absolutely impossible to filter in a day. His aim is to produce some large surface in the solution which will attract the precipitated sulphur, which otherwise would form round the zinc sulphide and so prevent the action of the iodine on the precipitate.

(B) *Ferrocyanide Titration*.—The direct titration of zinc solutions containing a small quantity of free acid by means of potassium ferrocyanide has been known fairly widely for a long time. Several workers have shown its weak and its strong points. The most important points are—first, the solutions in which a satisfactory result may be obtained; secondly, the influence of other metals; and

¹ Pouget, *Comptes Rend.*, 129 [1], 45–47.

² Knaps, *loc. cit.*

thirdly, the indicators employed. As regards the first of these, the solutions are limited to those containing a small quantity of free acid—one up to 3 per cent. of hydrochloric acid being quite suitable. The influence of the other elements has been considered fairly fully. Miller and Hall¹ show that lead interferes, though if 6 per cent. of hydrochloric acid be added the interference is rendered negligible. Antimony gives high results, but bismuth has no influence. Aluminium in any large quantities spoils the estimation,² and manganese acts similarly.³ In acid solutions magnesium has no effect. Calcium chloride has an effect upon the indicator if uranyl acetate is employed, as it dissolves the uranyl ferrocyanide. In ammoniacal solutions the precipitate is stated to be $\text{Zn}_2\text{Fe}(\text{CN})_6$, but in the acid solutions the precipitate is $\text{Zn}_3\text{K}_2(\text{Fe}(\text{CN})_6)_2$. In the third matter—of the indicator—it has been usual to employ uranyl acetate as the outside indicator. This always requires a certain excess of the potassium ferrocyanide to give the indication (up to 0.3 c.c. depending upon the volume of the solution). Some workers have tried to improve upon the spotting test by adding the indicator to the solution before commencing the titration. This is not a very great improvement, as the solution goes dark too rapidly from the start, and at the close of the titration is too dark to give any satisfactory end point, the finish being obscured rather than sharpened. The innovation is not to be recommended. Other indicators have been suggested—among them being ammonium molybdate. This has no particular advantage to offer over uranyl acetate.

The zinc solution should be quite free from ammonium thiocyanate (and if this is present it is advisable to use the iodimetric estimation rather than this with ferrocyanide, as the reagents employed to move the ammonium thiocyanate will cause more harm than good, besides which the removal will take up a great deal of time). Neutralise the solution with either ammonia or hydrochloric acid according as the solution is acid or alkaline, and arrange that finally

¹ Miller and Hall, *School of Mines Quarterly*, xvi., No. 3.

² Stone, *Journ. Amer. Chem. Soc.* (1895), xv. 473.

³ Low, *Journ. Amer. Chem. Soc.* (1893), p. 552.

there shall be about 3 per cent. of hydrochloric acid in solution. Heat this to the boiling point, remove from the plate, and titrate *at once*, running in the potassium ferrocyanide as rapidly as is safe. When the end point is approaching, it is advisable often to heat up again on the plate and finish at a temperature very near to the boiling point. Frequently the precipitate itself gives a fair indication of the near approach of the end point, as it settles down fairly rapidly, changing its habits quite suddenly, just before the end of the titration. Also there is a colour change from bluish white to white at the same time. The uranyl acetate is used on a tile.

The majority of analysts remove the nickel from German silver by the precipitation with dimethylglyoxime, and this always leaves an excess of the reagent and of alcohol in the solution. The removal of these is not an easy matter if the operator is in a hurry, and is quite unnecessary for the purposes of the ferrocyanide titration. As much as 100 c.c. of a 1 per cent. of dimethylglyoxime have no influence upon the titration, and do not affect the indicator.

CHAPTER XV

THE ANALYSIS OF COMMERCIAL ALLOYS

Brass.

BRASS consists essentially of copper and zinc, but it contains also small quantities of tin, lead, and iron, as well as traces of impurities such as arsenic. The alloy is readily decomposed by nitric acid or aqua regia, and comparatively large drillings or turnings can thus be used for analysis.

Determination of Tin.—The amount of tin in ordinary brasses is small ; if it exceeds, say, 2 per cent. as determined by the following method, the assay should be rejected, and the tin determined as described later under the analysis of bronze.

Treat 5 grams of the alloy with a mixture of 25 c.c. of nitric acid, sp. gr. 1.4 and 25 c.c. of water in a beaker. When decomposition is complete, evaporate the liquid to a volume of not more than 10 c.c., add 40 c.c. of hot water, and allow the liquid to stand for some minutes in a warm place. Filter out the hydrated stannic oxide through ashless paper pulp, washing with water containing a small quantity of nitric acid, and ignite, after drying rapidly at the mouth of the muffle, in a porcelain crucible. The residue is impure stannic oxide, containing 78.79 per cent. of tin.

The small amount of tin in commercial brasses renders the above method sufficiently accurate for ordinary purposes. If desired, however, the impure stannic oxide can be purified as follows. After weighing, add about ten times the weight of a mixture of equal parts of anhydrous sodium carbonate and flowers of sulphur, mix well by means of a rounded glass rod and heat the mixture over a small Bunsen flame, with the lid of the crucible in position. When the flame of burning sulphur between the crucible and lid just

disappears, allow to cool, and boil out the contents of the crucible with water. The aqueous extract contains the tin as sodium thiostannate, and traces of copper sulphide dissolved in the excess of sodium polysulphides resulting from the fusion. Add to the brown liquid a solution of sodium thiosulphate until a pale yellow colour only is left, and digest for some time to allow the sulphides of copper (lead and iron) to collect. Filter through pulp, and wash first with sodium sulphide water, and afterwards with hydrogen sulphide water. Dry and ignite. The weight of the ignited residue is deducted from that of the original stannic oxide.

Determination of Lead.—Lead is conveniently determined in the original filtrate from the hydrated stannic oxide, and also electrolytically (see the electrolytic determination of copper).

I. In the former case add about 10 c.c. of concentrated sulphuric acid to the solution, and evaporate until all nitric acid is expelled and fumes of sulphur trioxide are freely evolved. After cooling, add water in quantity sufficient to dissolve up the solid sulphates of copper and zinc (about 60 c.c.), and allow the lead sulphate to settle. The lead sulphate is then either weighed as such by collecting on a Gooch crucible as described on p. 52, or converted into lead molybdate as follows:—Pour the supernatant liquid through a small paper pulp filter, and wash the precipitate by decantation with dilute sulphuric acid (1 to 6). Dry the filter as much as possible by suction, and transfer to the beaker containing the remaining lead sulphate. Add 20 c.c. of hot ammonium acetate, 2 grams of ammonium chloride, a few c.c. of acetic acid, boil the solution along with the pulp and add a clear solution of ammonium molybdate. The lead is thus precipitated as PbMoO_4 , and this is filtered through another small pulp filter together with the original paper pulp, the whole washed with hot water, dried as much as possible by suction at the filter pump, transferred to a porcelain crucible and ignited.

$$\text{PbMoO}_4 \times 0.5640 = \text{Lead.}$$

II. An increase in the weight of the anode disc employed

in the electrolytic determination of copper described below is due to the deposition of peroxides of lead and manganese on it. These take the form of a brown or purple stain, or merely an iridescence. Having noted the increase in weight, dissolve the deposit by pouring a few drops of hot hydrochloric acid over it, and utilise the solution and washings for the

Determination of Manganese.—To the solution add a few drops of sulphuric acid, and expel the hydrochloric acid by evaporation to fumes of sulphur trioxide. Cool and add 10 c.c. of nitric acid, sp. gr. 1.20. Add next a few decigrams of sodium bismuthate, shake round, and allow to settle. If manganese is present, the supernatant liquid will show the characteristic colour of permanganates. Determine, if necessary, by filtering through asbestos, washing with 2 per cent. nitric acid until the washings are colourless, and titrating with a standard solution of ferrous ammonium sulphate. This is best done by adding a slight excess so as to discharge the permanganate colour completely, and then just reproducing a faint pink colour with a standard solution of potassium permanganate. The latter is used for standardising the ferrous solution, a suitable strength for such small quantities of manganese as are found in brass being N/50. Calculate the amount of manganese found to MnO_2 , and deduct from the total weight of the anodic deposit. The difference may be regarded without material error as PbO_2 , from which the lead percentage is calculated. See, however, *Electrolytic Determination* on p. 59.

Determination of Copper.—I. *Iodimetric.*—The iodimetric determination of copper can be applied directly to such alloys as brass, bronze, and German silver, and constitutes the best method for the estimation of the element.

Dissolve 0.5 gram of the alloy, contained in a conical flask, in about 10 c.c. of aqua regia, and boil off the excess of acid when solution is complete. Dilute to about 50 c.c. with water, and add a solution of sodium carbonate until the rest of the free acid is more than neutralised and a blue precipitate of basic carbonate of copper is obtained. Dis-

solve the latter in a slight excess of acetic acid B.P., boil to expel carbon dioxide, and then cool the liquid under the tap. (If more than traces of iron are present, a reddish scum of basic ferric acetate will be apparent, and this should be filtered out at this stage before proceeding with the determination of the copper.) Add about 2 grams of solid potassium iodide, shake round until the crystals dissolve, and allow the mixture of precipitated cuprous iodide and free iodine to stand for a few minutes. Deliver a decinormal solution of sodium thiosulphate from a burette, 1 c.c. at a time, with shaking of the flask, until the colour of the mixture becomes faintly yellow, add starch solution, and continue the addition of the thiosulphate until the colour is discharged. The change from the blue iodide of starch to colourless conditions is generally preceded by a momentary purple or red colour.

II. *Gravimetric*.—Weigh out 0.25 gram of the alloy, decompose with a few c.c. of nitric acid, remove any separated stannic hydrate, evaporate the filtrate, after the addition of 1 c.c. of sulphuric acid, to fumes, dilute, and filter out the lead sulphate. Add to the filtrate dilute ammonia until the solution is only feebly acid, then 20 c.c. of a saturated aqueous solution of sulphur dioxide, and finally a solution of from 1 to 2 grams of ammonium thiocyanate. Boil well, and allow the white precipitate of cuprous thiocyanate to settle for some time. Filter through pulp, wash with hot water, transfer to a porcelain crucible, dry and ignite to a mixture of cuprous sulphide and cupric oxide, containing 79.90 per cent. of copper. The results are not so reliable as those of the iodimetric method.

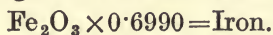
III. *Electrolytic*.—Dissolve 0.5 gram of the brass in 10 c.c. nitric acid (sp. gr. 1.41) in a small beaker, transfer to the weighed platinum dish, which is to serve as the kathode, and dilute with water up to about 150 c.c. Introduce the perforated platinum disc of Fig. 5, *b*, also previously weighed for the anode, and electrolyse at about 50° C. with a current density of about 1 ampere, or in the cold with 0.2 to 0.3 ampere, the voltage in either case being 2.5 to 3.5. In the latter case, start the action in the evening, and allow

to proceed until next morning. Consult Chapter V for fuller particulars.

The above procedure takes no notice of the hydrated stannic oxide resulting from the original decomposition with nitric acid. The amount of this, yielded by half a gram of an ordinary brass, is so little that its filtration is unnecessary. Much quicker deposition can be obtained by the use of heavier currents and rotating electrodes, and when a determination of the copper only is wanted, and that quickly, this form of the process is very useful. The authors are of opinion, nevertheless, that, for both quickness and accuracy, the iodimetric method is to be preferred. The particular merit of the electrolytic process lies in the incidental provision which it makes for a sufficiently accurate determination of lead and manganese, and also in the complete separation of copper from zinc, nickel, &c. The value of the latter is enhanced by the fact that the solution provided for the determination of zinc or nickel is free from sulphuretted hydrogen or dissolved solid reagents.

Determination of Zinc and Iron.—Of the methods described in Chapter XIV for the determination of zinc, the gravimetric phosphate method is the only one employed and recommended by the authors in the analysis of metallic alloys. Its application, like that of most others, necessitates the previous removal of copper, tin, and lead, an operation which is capable of execution in several ways, of which the following are the most important :

I. The solution and washings from the electrolytic determination of copper are concentrated as quickly as possible to a bulk of about 50 c.c. and the stannic hydrate, if any, filtered out and washed. Several grams of ammonium chloride are added to the filtrate, and then ammonia until the solution is alkaline. The liquid is digested until the ferric hydrate flocks together, and this is then filtered out, washed once or twice only with hot water, redissolved in a small quantity of hydrochloric acid, and re-precipitated with ammonia. The precipitate is filtered, washed thoroughly, dried, and ignited to ferric oxide.



Aluminium, if present, will be weighed up as alumina along with the ferric oxide, but the amount of it in ordinary brass or bronze is so small as not to require separation and determination. For the determination of zinc, the two filtrates and washings are combined, and the liquid again boiled down to a bulk of about 50 c.c. The acidity of the solution is then carefully adjusted, and the zinc precipitated as zinc ammonium phosphate and ignited to pyrophosphate exactly as described on p. 165.

II. 0.6 gram of the brass is decomposed with nitric acid, and tin, if present, removed. The filtrate is evaporated, after adding 2 c.c. of sulphuric acid, to thick fumes, and then about 100 c.c. of water added. The liquid is heated to boiling point and, without filtering out any separated lead sulphate, a brisk current of sulphuretted hydrogen is passed until the liquid is nearly cold. The copper sulphide precipitate and liquid are transferred together to a flask graduated at 120 c.c., and the volume made up by means of 1 per cent. sulphuric acid solution, previously saturated with sulphuretted hydrogen. After mixing, the liquid is filtered through a dry paper, and 100 c.c. of the filtrate, representing 0.5 gram of alloy, collected. The copper sulphide precipitate and the rest of the liquid are thrown away. The filtrate is boiled down to about 50 c.c. as quickly as possible, a few drops of concentrated nitric acid added, and the iron and zinc determined as before.

III. 0.6 gram of the brass is treated as in II, up to the separation of lead by fuming with sulphuric acid. In this case the lead sulphate is removed, after dilution with water containing sulphuric acid, by filtration, and the copper precipitated from the filtrate as cuprous thiocyanate. This is done as previously described by adding about 20 c.c. of saturated sulphur dioxide solution after most of the free acid has been neutralised with ammonia, and then an excess of ammonium thiocyanate to the hot liquid. After allowing to stand for some time, the precipitate and liquid are made up to 120 c.c. with water and 100 c.c. of the filtrate collected. The zinc and iron may be determined in the filtrate, after boiling off the excess of sulphur dioxide and concentrating to

about half the volume, by the usual methods. The authors prefer, however, to decompose the excess of ammonium thiocyanate before precipitating the iron and zinc. This is done by adding to the hot solution strong nitric acid, a few drops at a time, until the violent action, which each addition produces so long as there remains any undecomposed thiocyanate, ceases. The solution is then ready for the iron and zinc determinations.

Bronze

Bronze consists essentially of copper (80 to 90 per cent.) and tin, but it generally also contains zinc amounting to one or two units per cent., and also the usual impurities. The analysis of bronze differs from that of brass chiefly in the determination of tin. The difficulty of effecting a complete decomposition of relatively large amounts of ignited and impure stannic oxide by fusing with the sodium carbonate-sulphur mixture makes the ordinary method for the determination of tin of little value. The authors can confidently recommend the two following procedures.

Determination of Tin.—I. One gram of the drillings is attacked in a conical flask with about 10 c.c. of concentrated nitric acid, sp. gr. 1.4. (These amounts of material and of acid apply to the case of a bronze containing about 10 per cent. of tin—the amounts should be altered, according to circumstances, so as to provide about one decigram of tin.) The liquid is evaporated to a paste, about 75 c.c. of hot water added, and the mixture boiled for a few minutes. After allowing the precipitate to settle in a warm place, filter, whilst hot, through tightly packed asbestos, keeping as much of the stannic hydrate as possible behind in the flask, and washing by decantation with hot water containing a small quantity of nitric acid. There is no necessity to wash with any thoroughness, as the filtrate containing the copper must be discarded. It cannot be employed for the determination of the copper, as it does not contain it all, and the subsequent operations with the precipitate do not

allow of the recovery of the contained copper. The final washings are made with water until free nitric acid is removed, and then the filter and precipitate are transferred to the original flask containing the main part of the stannic hydrate, as little water as possible being used in the operation. An equal volume (about 20 c.c.) of concentrated sulphuric acid is then added, and the mixture boiled as vigorously as possible, having due regard to bumping, for about three minutes, after which time 50 c.c. concentrated hydrochloric acid are added. After boiling for about two minutes, perfect solution of the tin precipitate is obtained, though this is not easy to see by virtue of finely divided particles of asbestos. About 1 gram of antimony powder is then added, the liquid boiled for a minute vigorously, cooled in a current of carbon dioxide, and the tin determined by titration with $\frac{N}{20}$ iodine solution, as described in Chapter VIII.

$$1 \text{ c.c. } \frac{N}{20} \text{ iodine solution} = 0.002975 \text{ gram tin.}$$

The above method gives excellent results provided the stated proportions of the two acids are not altered appreciably.¹

II. Half a gram of the drillings is dissolved in 10 c.c. of aqua regia, and the solution diluted with an equal volume of water. A solution of sodium hydrate is added until most of the free acid is neutralised without the formation of a precipitate, and the mixture is then heated to boiling. In a large conical flask 20 grams of sodium hydrate are dissolved in about 300 c.c. of water, and this solution is also heated to boiling, whereupon 2 to 3 grams of hydrazine hydrochloride are added to it. The mixture of cupric and stannic chlorides is then transferred to a separating funnel, and is delivered in drops into the strongly alkaline solution, whilst the latter is being vigorously shaken. The copper is precipitated as metal, with previous, but momentary, formation of its lower oxide. The mixture is now

¹ *Chem. News*, 107, 109.

digested for about 15 minutes until the vigorous evolution of gas subsides, the metallic copper is filtered out and washed with hot water. The tin is determined either gravimetrically or volumetrically in the filtrate. In the former case, add hydrochloric acid until the liquid is distinctly acid, concentrate to much smaller bulk by evaporation, and precipitate as stannic sulphide under the necessary conditions of acidity, collect the precipitate, and convert to stannic oxide as described in Chapter VIII. In the latter case, the filtrate is also acidified, concentrated, and sufficient strong hydrochloric acid added to produce the required degree of acidity for reduction with floured antimony and subsequent titration with $\frac{N}{20}$ iodine. The precipitated copper can be used for the determination of that element.

Determination of Lead.—Proceed as described under the analysis of brass, Method I.

The results are slightly low, because the much larger amounts of stannic oxide yielded by a bronze contain correspondingly greater amounts of occluded lead.

As an alternative, dissolve 5 grams of the drillings in a mixture of 40 c.c. of hydrochloric acid with 10 c.c. of nitric acid (1.4), and evaporate, after adding 20 c.c. concentrated sulphuric acid, to copious fumes of sulphur trioxide. After cooling, add 40 c.c. cold water, stir until the copper sulphate passes into solution, and allow the separated lead sulphate to settle. This is then collected or transformed to molybdate as previously described. The latter treatment is recommended so as to eliminate small quantities of stannic hydrate associated with the lead sulphate.

Determination of Copper.—I. Iodimetrically, as in brass.

II. The metallic copper, obtained in the “hydrazine separation” of this element from tin, is dissolved from the filter with a hot mixture of equal parts of 1.20 nitric acid and water, and the copper determined iodimetrically as before.

Determination of Zinc.—Copper, tin, and lead are removed as described under the analysis of brass, the electrolytic method being the most suitable, but the solution from the

electrolysis must be concentrated to a volume not exceeding 20 c.c., if a satisfactory determination of the relatively small amount of zinc (and iron) is to be made by the "phosphate method." Or, the zinc (and iron) are precipitated from the solution after making alkaline by means of hydrogen sulphide or ammonium sulphide, the precipitate collected and washed, dissolved in dilute hydrochloric acid, the solution boiled well so as to expel hydrogen sulphide and effect concentration, and the metals determined as before.

Manganese Bronze

Nearly all the alloys which are designated by the term "manganese bronze" contain less than 1 per cent. of manganese, though certain special ones contain as much as a fifth to a quarter of their own weight of this element. Their analysis presents no difficulties, as it does not differ essentially from that of an ordinary bronze or brass with respect to the determination of tin, copper, lead, &c. The following instructions will be found useful in connection with the

Determination of Manganese.—I. The whole of the manganese is obtained from low-percentage alloys as a deposit of peroxide on the anode in the electrolysis of a nitric acid solution of the alloy. This case is dealt with under the analysis of brass.

II. The alloy (1.32 gram) is opened out with aqua regia, evaporated to fumes with sulphuric acid, the residue taken up with water, the solution saturated with hydrogen sulphide, the liquid and precipitate made up with hydrogen sulphide water to 120 c.c., and 100 c.c. of solution (representing 1.1 gram of the alloy) filtered off through a dry filter paper. The filtrate is boiled to expel the excess of hydrogen sulphide and to reduce the volume to about 50 c.c., and then treated (a) for the determination of manganese only, or (b) if required, for the determination of iron as well.

(a) Add 20 c.c. of concentrated nitric acid, cool the

solution to 20° C. or less, add 1 gram of sodium bismuthate, shake, allow to settle, filter through asbestos, wash with 5 per cent. nitric acid, and titrate the "permanganate" in the filtrate with decinormal ferrous ammonium sulphate solution in the manner described on p. 173. Each c.c. of ferrous solution is equivalent to 0.0011 gram of manganese and registers 0.01 per cent. of manganese.

(b) Add 5 c.c. of bromine, shake until dissolved, and make distinctly alkaline with ammonia. Digest or boil until the precipitate flocks out, filter, wash with hot water, dry, ignite in a platinum crucible, and weigh as $\text{Fe}_2\text{O}_3 + \text{Mn}_3\text{O}_4$. (The ignited residue may also contain alumina and negligible traces of zinc.) Brush the residue into a conical flask, add 10 to 20 c.c. HCl, heat until solution is effected, and evaporate to fumes after the addition of 5 c.c. of sulphuric acid. Take up again with 1.20 nitric acid, determine the manganese as in (a), calculate the amount found to Mn_3O_4 , and deduct from the weight of the mixed oxides. The difference gives the ferric oxide (and alumina):

III. The alloy is decomposed with strong nitric acid and water, and the tin removed as previously described. The filtrate is treated with bromine and ammonia, the precipitated hydroxides filtered out, washed, ignited, dissolved in hydrochloric acid, evaporated to fumes with sulphuric acid, the residue taken up with 1.20 nitric acid, and the assay for manganese finished as in II.

In this case the precipitated hydroxides are contaminated with copper, which may subsequently impart a colour to the nitric acid solution of the ignited residue. The intensity of the colour is, however, never great enough to affect seriously the determination of the end point of the titration.

IV. The alloy is decomposed with nitric acid as before, the tin removed, and the bismuthate determination applied directly to the filtrate. In this case a solution of the same depth of colour, made by dissolving copper nitrate in water, is used for comparison with the assay, so as to assist in deciding the end of the titration.

Phosphor Bronze

Phosphorus, like manganese, is added to bronzes during their manufacture, for purposes of oxidation, and small quantities remain in the solid alloy. The purposed addition of larger amounts for making certain castings justifies the use of the term "phosphor bronze," which appears, however, to be applied to any bronze in the manufacture of which phosphorus has been employed. This is evident from the fact that many of them on analysis show traces only of this element. It has already been pointed out on p. 101 that the so-called metastannic acid resulting from the decomposition of an alloy containing tin by means of nitric acid exerts an adsorptive effect on phosphoric acid, and if, as is almost always the case, the amount of tin in the alloy is at least from five to eight times the amount of phosphorus, the whole of the non-metal is present in the insoluble residue.

The determination of tin by Method I (*q.v.*) in phosphor bronze is not affected by the presence of the "stannic phosphate" in the insoluble residue, nor does the presence of phosphorus affect the accuracy of the "hydrazine method." The other metallic constituents also require no further treatment. Of the following methods for the determination of phosphorus, the first does not differ from that of Oettel¹ in the separation of the tin from the phosphoric acid, but only in the actual determination of the phosphorus. The second is a modification of the method of Dudley and Pease; the third, which is easier of manipulation, gives equally satisfactory results.

I. Five grams of the alloys of low phosphorus percentage are decomposed with nitric acid, and the insoluble residue collected, dried, and ignited in a porcelain crucible. The impure residue is well mixed with three times its weight of potassium cyanide, the crucible covered, and the mixture ignited. The products of the fusion are metallic tin and potassium phosphate, along with cyanate and cyanide of

¹ Oettel, *Chem. Zeit.* (1896).

potassium. By careful manipulation of the crucible during the ignition, most of the particles of tin can be collected into one bead, particularly if the fusion is conducted in a crucible with a rounded bottom. After cooling, the melt is extracted with water, the metallic tin strained off, and the filtrate acidified with hydrochloric acid. The solution is boiled in the fume cupboard until hydrogen cyanide is eliminated, and the traces of tin and copper precipitated with a current of hydrogen sulphide. The filtrate from the sulphides is boiled until all the excess of sulphuretted hydrogen is removed, and it is then ready for the determination of the phosphorus. In the original recommendations, this was done by precipitation with magnesia mixture and ignition to pyrophosphate.

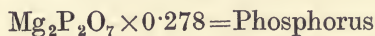
The authors prefer to remove the phosphoric acid from the solution by adding a solution of ferric nitrate made by dissolving about one decigram of Swedish bar iron in 1.20 nitric acid, and then precipitating with ammonia. The precipitated ferric phosphate and hydroxide are filtered out, washed with hot water, and then dissolved from the filter with 40 c.c. of hot 1.20 nitric acid. Five c.c. of ammonia, sp. gr. 0.880, are added, the precipitate which forms, dissolved in the excess of acid, and 30 c.c. of ammonium molybdate reagent added. The mixture is kept at 70° to 80° C., with occasional shaking, to allow the ammonium phosphomolybdate to precipitate completely. The precipitate is then collected on a tared filter paper or Gooch crucible, washed with 2 per cent. nitric acid, dried at 100° C., and weighed as $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$, which contains 1.65 per cent. of phosphorus.

The yellow precipitate may also be converted to lead molybdate, and the authors strongly recommend this, by the following series of operations, which are much more quickly effected than a perusal of them would lead one to expect. The precipitate is collected on a filter of paper pulp, washed thoroughly with cold 2 per cent. nitric acid, and then dissolved off into a conical flask with 4 c.c. of ammonia 0.880, followed by hot water. The liquid is again passed through the filter, and received in a similar

flask along with the hot water rinsings of the other. The liquid is then heated to boiling, and also a mixture in the now empty flask of 50 c.c. of ammonium acetate with 10 grams of ammonium chloride dissolved in water. When both solutions boil, the former is acidified with 10 c.c. concentrated hydrochloric acid, 10 c.c. of a 4 per cent. aqueous solution of lead acetate added immediately, and the mixture poured at once into the other flask containing the ammonium acetate-chloride solution. Lead molybdate is precipitated, and is at once filtered through "ashless" paper pulp, washed with hot water, sucked as dry as possible at the filter pump, and ignited without further drying. The weight of the ignited residue, multiplied by 0.007, gives the actual weight of phosphorus in the original precipitate of ammonium phospho-molybdate.

The specified quantities of the various reagents used in the second part of the above process are not suitable for larger percentages of phosphorus than 0.04, when 5 grams of the alloy are used, representing an actual weight of two milligrams. This does not apply to the operations prior to the precipitation of the ammonium phospho-molybdate, which are common to high as well as low phosphorus alloys. The maximum amount of phosphorus rarely exceeds 0.5 per cent., and it is advisable either to start with a much smaller amount of these richer alloys in the first instance, or to dissolve the ammonium phospho-molybdate in larger amounts of ammonia, and proceed with a measured aliquot portion of the filtrate arranged to hold 4 c.c. of the ammonia and an amount of phosphorus lower than the specified limit of 2 milligrams. Small as this amount is, it must be remembered that the weight of lead molybdate which it finally yields is nearly 290 milligrams, which is quite sufficient to handle with ease and rapidity. The reason for the limitations imposed lies in the fact that the addition of hydrochloric acid to the ammoniacal solution of the yellow precipitate results in a precipitation of phospho-molybdic acid from solutions of richer phosphorus content, and the transformation of this into lead molybdate by the subsequent operations is not so readily brought about.

II. The alloy is dissolved in a mixture of equal volumes of nitric (1·4) and hydrochloric acids at the rate of 20 c.c. per gram of alloy, and the solution boiled for 10 to 15 minutes. It is then cooled, diluted with about twice its own volume of water, and ammonia added until the precipitate which forms just redissolves to produce the characteristic deep blue solution. Colourless ammonium sulphide is then added until, after stirring and allowing to settle, the supernatant liquid is quite colourless. The mixture is digested just short of boiling for 15 minutes, the sulphides of copper and lead allowed to settle, and the clear liquid decanted and filtered through paper. The precipitate is also transferred to the filter, allowed to drain, and then transferred to the original beaker together with the filter. Diluted ammonium sulphide is poured over the precipitate, and the mixture heated for some minutes with occasional stirring; it is then filtered through another paper, and well washed with more hot dilute ammonium sulphide. The filtrate and washings, occupying a bulk of about 250 c.c., are treated with magnesia mixture, the vessel placed in ice-water mixture, and shaken occasionally over a period of two hours. The precipitated ammonium magnesium phosphate is then collected, washed with dilute ammonia, and then dissolved in as little hydrochloric acid as possible. The phosphoric acid is then reprecipitated under the usual conditions, washed, dried and ignited to magnesium pyrophosphate.



III. The alloy is decomposed with nitric acid as usual, the liquid decanted as completely as possible from the insoluble residue, and poured through an asbestos filter. The residue is washed, also by decantation, so as to accumulate as little of the precipitate as possible on the filter. About 25 c.c. of concentrated hydrochloric acid, heated to boiling, are then poured through the filter and received in the flask containing the main portion of the "stannic phosphate" residue. The liquid is heated just short of boiling until complete solution is effected, more acid being added if required. The clear solution is then poured through the

asbestos filter again, so as to dissolve the last traces of the precipitate, and the filter washed once or twice with more hot acid. The filtrate is diluted as largely as possible with water, consistent with the retention of the tin in solution, and the metal is then precipitated as such by the introduction of a rod of pure zinc. After straining off the metallic tin, the solution containing the phosphoric acid is then dealt with exactly as in Method I.

Aluminium Bronze

The aluminium contents of this alloy vary between 1 and 12 per cent.; the remainder consists essentially of copper and small amounts of silicon.

Determination of Silicon.—Dissolve 2 grams of the alloy in 20 c.c. of aqua regia, add 10 c.c. of concentrated sulphuric acid, and evaporate to fumes of sulphur trioxide. Take up the residue in water, filter through "ashless" paper pulp, wash, dry and ignite in a platinum crucible. The silica thus obtained is free from copper, but may contain lead sulphate and traces of stannic oxide. It is therefore treated with hydrogen fluoride and a few drops of sulphuric acid, heated gently at first to expel silicon tetrafluoride, more strongly afterwards to remove the excess of sulphuric acid, and finally ignited at redness. The loss in weight is taken as silica, which contains 46.93 per cent. of silicon.

Determination of Copper.—Apply the iodimetric or electrolytic methods as described under brass.

Determination of Aluminium.—The determination of this element necessitates the previous removal of copper, for which several methods are easy of application. The filtrate from the silicon determination, for example, may be utilised directly and the copper precipitated (*a*) by hydrogen sulphide, (*b*) by sodium thiosulphate, and (*c*) by ammonium thiocyanate. The usual time-saving device of fractional filtration should be resorted to in each case. The electrolyte remaining from the determination of copper also provides a suitable solution for the same purpose. Of the

first three, the sulphuretted hydrogen precipitation provides a filtrate most suitable for the determination of aluminium.

It is only necessary to expel the excess of hydrogen sulphide from it, and, without filtering out any sulphur which separates, apply the phosphate method described in full on p. 139 to the solution, due regard being paid to the quantities of reagents specified for a given amount of aluminium.

The nitric acid solution from the electrolytic deposition of copper is obviously easily adaptable to the same process. In this case, however, the ignited aluminium phosphate contains silica, the amount of which must be deducted after its determination *via* hydrofluoric and sulphuric acid.

Phosphor Tin

This alloy contains, as a rule, about 5 per cent. of phosphorus, and constitutes the vehicle by which the non-metal is generally introduced in the manufacture of phosphor bronze. The analysis for the two essential constituents presents no special difficulties, and might be dismissed without further consideration, but for the fact that the decomposition of phosphor tin by concentrated hydrochloric acid results in the complete expulsion of the non-metal in the form of its gaseous hydride. Gemmel and Archbutt,¹ taking advantage of this fact, determine the phosphorus by an evolution method, of which the following is a brief outline:—The alloy is placed in a flask provided with a two-way tap funnel and delivery tube, which leads to three absorption bottles, the first two containing bromine and bromine water, and the last bromine only. The air is expelled from the apparatus by a current of carbon dioxide and concentrated hydrochloric acid run into the flask, whereupon the application of gentle heat results in complete solution of the alloy, accompanied by visible reduction of bromine in the absorption apparatus.

¹ *Journ. Soc. Chem. Ind.* (1908).

The liquid in the decomposition flask is raised to boiling when solution is complete, and any phosphine left in the flask swept out finally by carbon dioxide. The absorption vessels are then washed out into a large beaker, the excess of bromine expelled, and the phosphoric acid determined in the usual manner as magnesium pyrophosphate.

German Silver

The composition of German silver varies between the following approximate limits—copper 50 to 66 per cent., zinc 19 to 31 per cent., and nickel 7 to 30 per cent. Tin and manganese occur generally as traces only, but lead and iron are almost invariably present in small but variable amounts. German silver is one of the few non-ferrous alloys which lend themselves readily to the easy determination of almost all the constituent metals out of one original weighing. This does not, of course, prejudice the value and importance of separate determinations of single elements, and particularly that of nickel, which is of primary importance.

Determination of Copper.—I. Apply the iodimetric process as described under brass.

II. Deposit the copper electrolytically from nitric acid solution of the alloy; any peroxide deposit on the anode should be weighed, dissolved off, and tested for manganese, and the lead taken by difference.

Determination of Lead.—The electrolytic determination can be supplemented by the gravimetric determination as sulphate or molybdate.

Determination of Nickel.—I. The precipitation of nickel from ammoniacal solutions by means of dimethylglyoxime is by far the best method for the determination of this element in German silver. The method can be applied directly,¹ since zinc and copper are retained in solution by an excess of ammonium hydrate.

Dissolve not more than half a gram of drillings in 10 c.c.

¹ *Chem. News*, 104, 224.

of nitric acid (1·20), filter if the solution shows a turbidity due to tin, and dilute to about 400 c.c. with water. Add a few decigrams of tartaric acid to retain small quantities of iron in solution, and add ammonium hydrate until the deep blue solution indicates a distinct excess. Heat to about 50° C., and add an excess of a solution of dimethylglyoxime in alcohol. (The amount of the solid reagent should be approximately four times that of the nickel.) Allow the mixture to stand in a warm place, with occasional stirring, for 15 minutes, collect the voluminous red precipitate on a folded paper, and wash with hot water containing ammonium nitrate until the washings are colourless. As thus obtained, the precipitate is not quite free from copper, and it is therefore dissolved from the filter with a warm mixture of equal volumes of 1·20 nitric acid and water, and the precipitation repeated. The precipitate is then either collected on a weighed Gooch crucible, dried at 100° to 105° C., and weighed as $\text{NiC}_8\text{H}_{14}\text{N}_4\text{O}_4$, containing 20·32 per cent. of nickel, or on ashless pulp and ignited with the precautions specified on p. 150 to NiO , containing 78·59 per cent. of nickel.

II. The volumetric determination of nickel by titration with potassium cyanide and a silver iodide indicator cannot be applied without previous removal of copper, as this element also reacts with potassium cyanide. Zinc also exerts a disturbing influence, which, however, can be counteracted by the introduction of sodium pyrophosphate. The following procedure gives results which are approximately accurate, but quickly secured.

The copper and lead are removed by electrolysis of a nitric acid solution of half a gram of the alloy, and the solution transferred to a beaker and largely diluted. Four grams of ammonium chloride and the same quantity of sodium pyrophosphate are dissolved in the solution, which is then rendered faintly but distinctly alkaline. Potassium iodide solution is added, a few c.c. of a standard solution of silver nitrate, and the titration with potassium cyanide followed by standardisation of the latter, conducted as described on p. 151.

Complete Analysis of German Silver

The following excellent scheme, due to Spring,¹ can be confidently recommended.

Half a gram of drillings is dissolved in nitric acid, stannic hydrate, if present, removed by filtration, the solution evaporated to fumes with sulphuric acid, and lead sulphate removed. The solution of sulphates and free sulphuric acid is then electrolysed under the necessary conditions (*q.v.*), the copper being thus removed and determined. The iron is next removed from the solution by means of ammonia, the filtrate treated with 5 grams of ammonium chloride, nearly neutralised with hydrochloric acid, and a solution of dimethylglyoxime in alcohol (4 decigrams of the solid per decigram of nickel) added, and the whole mixture made slightly ammoniacal. Half an hour at a temperature near the boiling point is allowed for complete precipitation of the nickel before filtering. The precipitate is dried at 105° C., and weighed. Before proceeding to the determination of zinc in the filtrate, the latter should be treated with a few more drops of the alcoholic solution of the reagent to ascertain whether precipitation of the nickel was complete. Incomplete precipitation is indicated by a reddening of the solution. The zinc is determined by acidifying the filtrate with hydrochloric acid, adding 10 c.c. more in excess, boiling well to decompose the excess of dimethylglyoxime reagent, and precipitating as zinc ammonium phosphate after readjusting the acidity of the solution.

The only modification of the above which the authors use consists in electrolysing the original nitric acid solution of the alloy, thus obtaining the copper and lead in one operation. The liquid is then filtered from any stannic hydrate before proceeding as above.

Lead, Antimony, Tin Alloys

The above heading is intended to embrace a large number of alloys of vastly differing composition and properties,

¹ *Chem. News*, 104, 58.

such as Babbitt metals, Magnolia metal, pewter, solders, type metal, bearing and anti-friction metals, &c. The loose term "white metals," which is frequently applied to these alloys, does not include the commercially important alloys of aluminium with zinc and with magnesium; these are generally called "light metal alloys." Many of the "white metals" contain no antimony at all, and some no lead, but very few are free from tin; copper up to a few units per cent. is a constituent of frequent occurrence, and one or two special alloys contain comparatively large amounts of zinc.

The number of schemes for the complete analysis of white metal alloys is an increasingly large one, but it is difficult to find a method which can be successfully applied by other than the skilled worker. This is obviously a consequence of the fact that the authors of such schemes are in many cases concerned with a particular alloy or class of alloys. The fact that many alloys contain as much as 80 or even 90 per cent. of one metal only determines their analysis along the lines of that universally adopted for iron and steel, converting it perforce into a series of separate determinations. Whilst, therefore, an outline of a semi-complete scheme for the analysis of white metal alloys is appended, the authors recommend the application of the other method of procedure, and particularly with respect to lead, antimony, and tin.

The wide variation in the composition of these alloys is manifested in their behaviour towards the usual reagents employed in "opening-out." Aqua regia is an effective solvent in nearly every case, but when the subsequent operations preclude its employment, decomposition is sometimes prolonged, and the question of sampling is of importance in this connection. Fortunately white metals are extremely soft, so that filings or "sawings" can readily be obtained. The authors use filings obtained by rubbing the alloy along the flat surface of a medium-cut file, which is easily cleaned after sampling by means of a "scratch-brush." The fear of serious contamination of the filings with iron is groundless.

Determination of Lead.—I. One gram of the alloy is weighed, transferred to a wide test-tube or narrow beaker, and digested with 20 c.c. of hydrochloric acid until action nearly ceases. The residue is then taken into complete solution by means of a rapid current of chlorine gas, the liquid being kept at or near the boiling point during the operation. When a clear solution is obtained, it is transferred to a glass dish and evaporated to pastiness. The residue is treated with alcohol, stirred well, and the lead chloride collected as described on p. 54.

$$\text{PbCl}_2 \times 0.7451 = \text{Lead}$$

II. One gram of the filings is treated with 20 c.c. of aqua regia, and, when solution is complete, a solution of 2 grams of tartaric acid in water is added, followed by 10 c.c. of sulphuric acid. The mixture is then evaporated to complete expulsion of the excess of the more volatile acids, and the lead sulphate filtered out and determined as described on p. 52. It is necessary to watch the evaporation towards the finish, because, if it proceed too far, charring sets in. The point at which the nitric and hydrochloric acids are driven off is marked by the cessation of red fumes and a sudden quiescence in the mixture.

$$\text{PbSO}_4 \times 0.6831 = \text{Lead}$$

Determination of Copper.—The determination of copper by any method which does not involve a previous separation is generally unsatisfactory. Copper can be quantitatively precipitated and separated as sulphide from antimony and tin by means of sodium sulphide or sulphuretted hydrogen in alkaline solution, also from antimony, tin, lead, and zinc by means of hydrazine hydrochloride in strongly caustic alkaline solution. The former case is dealt with later in the scheme for the complete analysis of white metals, and the latter operation is performed as immediately follows: ¹

0.5 gram of the alloy is treated with about 15 c.c. of aqua regia, an equal volume of water added when solution is complete and the mixture cooled. If crystals of lead chloride separate, they are strained off through a small

¹ *Chem. News*, 107, 121.

filter of paper pulp and washed several times with small quantities of cold water. One gram of tartaric acid is dissolved in the filtrate, and sodium hydrate solution then added until the solution is nearly neutral. The liquid is then heated to boiling, and run from a separating funnel in drops into a hot solution of 20 grams of sodium hydrate and 2 to 3 grams of hydrazine hydrochloride in 250 to 300 c.c. of water. The latter is agitated briskly during the operation. The mixture is then heated for about 15 minutes, at the end of which time evolution of gas will have nearly ceased and the metallic copper collected in dense flocks. The metal is filtered through paper pulp and well washed with hot water. It is then dissolved off in a hot mixture of equal volumes of 1.20 nitric acid and water, and the copper determined iodimetrically.

Determination of Antimony.—The gravimetric determination of antimony either in the form of sulphide or tetroxide is of little value, in the analysis of alloys, in comparison with the volumetric methods, which are equally accurate and much more quickly executed. The fact that tin is an almost invariable constituent of these alloys necessitates a separation, usually by means of hydrogen sulphide in suitably adjusted solutions, before antimony can be determined gravimetrically. On the other hand, the volumetric determinations *via* potassium bromate or iodine monochloride can be made accurately in the presence of tin and other elements as well, with limitations, and are therefore applicable directly to the majority of white metals.

I. *The "Bromate Method."*—One gram of the sample is dissolved by means of about 25 c.c. of hydrochloric acid, with the occasional addition of a crystal or two of potassium chlorate, or in the same acid together with a saturated solution of bromine in it, also added from time to time. The excess of chlorine or bromine is expelled and the antimony reduced to trichloride by boiling to low bulk with a few grams of sodium sulphite. The acidity of the solution is then adjusted, any traces of sulphur dioxide expelled, and the assay finished as described on p. 93.

Lead, tin, and zinc are without effect, but the results are vitiated by the presence of copper if present to the extent of more than 3 per cent.

II. *The "Iodine Monochloride Method."*—The accuracy of this method does not appear to be impaired by the presence of lead, antimony, copper, and zinc. As described fully on p. 95, it can be applied to the solution obtained after "opening-out" with hydrochloric acid and potassium chlorate, expulsion of chlorine and reduction of the antimony pentachloride as described in the same place.

III. When a white metal alloy is decomposed with a large excess of dilute hydrochloric acid in the presence of potassium iodide, the residue which is left when action just ceases contains all the antimony. An approximate determination of the metal can thus be made by simply collecting the residue on a weighed Gooch crucible, washing with dilute hydrochloric acid, then with alcohol, drying at 100° C., and weighing as metal. This method, as a matter of fact, has been recommended by several observers. The authors find, however, that the residue thus obtained is frequently not quite free from lead and copper, and the removal of these by allowing the mixture to stand for too long a time after action has ceased, leads, on the other hand, to low results, presumably because antimony slowly passes into solution.

For the effective removal of the greater portions of tin, lead, copper, &c., with a view to the subsequent volumetric determination of the antimony, the process is invaluable. The following are the details.

One gram of the sample is covered with 40 c.c. concentrated hydrochloric acid and 40 c.c. of water containing one gram of potassium iodide, and the mixture kept hot until action is nearly, but not quite at an end. The metallic antimony with the small amount of impurities is then filtered through asbestos and washed well with dilute hydrochloric acid. The residue is then dissolved from the filter with hydrochloric acid in which potassium chlorate has been previously dissolved, and the solution boiled to expel chlorine. The pentachloride of antimony is then reduced, and the metal determined as above or by titration with iodine after the

usual adjustment of the solution to alkalinity with sodium bicarbonate.

Determination of Tin.—Tin, like antimony, is much more satisfactorily determined in alloys volumetrically than gravimetrically. An indirect gravimetric assay of approximate accuracy is made by finding the weight of the mixed oxides of tin and antimony yielded by decomposition of the alloy with nitric acid, and determining the antimony in a separate sample. Yockey¹ dissolves 1 gram of the alloy in dilute nitric acid (1 : 2), evaporates to dryness, and heats the dried residue for an hour at 120° C. He then moistens with nitric acid and boils up with 40 c.c. of water, collects the residue, ignites and weighs as $\text{Sb}_2\text{O}_4 + \text{SnO}_2$. In another 1-gram sample he determines the antimony by treating with a mixture of 40 c.c. hydrochloric acid, 40 c.c. of water, and 1 gram of potassium iodide, the residue of metallic antimony being collected on a tared filter, washed with dilute hydrochloric acid (1 : 10), then with water and alcohol, and finally dried and weighed as metal. The weight so found is then calculated to Sb_2O_4 , and subtracted from the weight of the mixed oxides.

The volumetric methods consist in the titration of stannous chloride in hydrochloric acid by means of iodine or ferric chloride solutions.

I. *Titration with Iodine.*—(A) Tin can be determined directly in alloys containing less than 5 per cent. of copper and traces only of arsenic without serious error. As the majority of alloys conform to these conditions, the method is capable of extensive application. One gram of the alloy is opened-out with hydrochloric acid and potassium chlorate, and when solution is complete, the liquid is cooled. Should this result in the deposition of lead chloride in quantity, the liquid is filtered through pulp, and the filtrate and washings made up to a definite volume. An amount of solution estimated to contain between 1 and 2 decigrams of tin is measured out in the case of rich tin alloys, and this is diluted with water and hydrochloric acid so as to produce the conditions described on p. 106. The assay is then finished as there described.

¹ *Journ. Amer. Chem. Soc.* (1906), 28, 646.

(B) The method of eliminating a metal from solution by the introduction of another whose presence is without influence on subsequent operations, is extensively practised by many analysts, and in connection with the determination of tin in alloys is of considerable value. The disturbing influence of copper on the above method, for example, can be obviated by its complete removal in this manner. The following summary of metallic precipitations, which only includes the metals usually encountered in the alloys under consideration, will be found useful in this connection.

Copper precipitates arsenic and antimony, but not tin.

Iron precipitates antimony and copper, and reduces ferric and stannic chlorides.

Tin precipitates arsenic, antimony, and copper.

Aluminium precipitates copper, antimony, iron, and zinc.

Zinc precipitates tin, antimony, copper, lead, and arsenic, the latter being in part converted into and evolved as arsine. The modification of Method (A), which the introduction of the changes which this principle imposes, yields excellent results; the following are the details.

Dissolve as before in hydrochloric acid and potassium chlorate, dilute with about an equal volume of water, and insert a clean iron rod. Cover and allow to simmer gently until the solution is colourless, remove and wash the iron rod, and filter. Adjust the acidity of the filtrate, boil with metallic antimony to complete the reduction, and titrate after cooling in a current of carbon dioxide. Alternatively, reduce by adding a decigram or two of fine iron wire, allow to remain until dissolved, cool and titrate as before.

II. *Titration with Ferric Chloride.*—Titration of stannous chloride in strong hot hydrochloric acid solution is a convenient method for the determination of comparatively large amounts of tin, and is therefore applicable to rich tin alloys. The preliminary operations described under the iodine titration, Method (B), are the same in each case, and the titration is fully described on p. 107.

The precipitation of the constituent metals by the introduction of others is strongly advocated by Parry,¹ who

¹ *The Assay of Tin and Antimony*—Mining Journal Office.

eliminates the tin itself in this way before titrating with ferric chloride. The alloy is decomposed with hydrochloric acid and potassium chlorate, antimony and copper precipitated from the hot acid solution by means of iron wire, and a strip of metallic copper introduced to precipitate arsenic. The liquid is then diluted and filtered, an excess of zinc added and allowed to remain until action ceases. The precipitated tin and zinc are then collected and washed into a flask with a large excess of concentrated hydrochloric acid. Another small piece of zinc is then introduced, and the metals completely dissolved by boiling. The hot solution is then at once titrated as quickly as possible with the ferric chloride solution.

General Analysis of White Metal Alloys

One gram of the finely divided alloy is attacked, in a conical flask covered with a watch-glass, with 20 c.c. of concentrated hydrochloric acid, and the action allowed to proceed short of boiling until nearly at an end. Tin, lead, and zinc are taken almost completely into solution, and the insoluble residue contains the antimony and most of the copper. Solid potassium chlorate is added in very small quantities at a time until the residue, the amount of which has been mentally noted, is taken into solution, whereupon the excess of chlorine is expelled. The solution thus obtained is yellow, and the intensity of the colour furnishes a rough estimate of the amount of copper present. The liquid is cooled off rapidly under a stream of water when, in the case of alloys rich in lead, an abundant crop of crystals of lead chloride falls out. These crystals are strained off through a small asbestos filter, washed with small quantities of cold water (the washings being collected in the filtrate), and are then dissolved from the filter with hot dilute hydrochloric acid. The solution is then evaporated to fumes with sulphuric acid, the lead sulphate collected in the usual manner, and its amount added to that subsequently recovered from the original filtrate. The latter, or the original solution in the event of no separation of lead chloride, is diluted

to about 80 c.c., from 1 to 4 grams of tartaric acid, according to the size of the residue left after the first decomposition with hydrochloric acid, added, and a solution of pure sodium hydrate added until the liquid is distinctly alkaline.

The solution, the blue colour of which betrays copper and its approximate amount, is usually clear, but may be slightly turbid. After heating to about 90° C., a saturated solution of freshly prepared hydrogen sulphide water or a solution of colourless sodium sulphide is added in not too large an excess. As it is important to avoid large excesses of these reagents, their addition is made carefully, with constant stirring of the mixture. By so doing, the "flocking-out" of the sulphides of lead, &c., is promoted, and they settle rapidly, leaving a supernatant liquid. When the latter is clear and colourless, and remains so on further testing with a few more drops of either reagent, the precipitate is collected on paper, and washed with water containing a little sodium sulphide until acidification of the washings shows the absence of tin and antimony. Filtrate and washings are received in a capacious beaker.

The Filtrate.—The alkaline filtrate contains the antimony and tin and the small quantity of arsenic usually present in most alloys. The determination of the latter should not be attempted in this solution; its amount, operating on one gram only of the alloy, is negligible so far as it affects the remainder of the analysis.

The next operation is conditioned by the method to be employed in the subsequent separation of the antimony and tin. For this purpose the authors prefer a solution as free as possible from unnecessary dissolved salts, and they re-precipitate the sulphides of tin and antimony by adding hydrochloric acid until the solution is distinctly acid, a large excess being avoided. On digestion, the sulphides readily flock out, but it is unsafe to regard the precipitation as complete, and a current of sulphuretted hydrogen should be passed through the warm solution during the digestion. As much as possible of the supernatant liquid, after the precipitate has settled, is poured through a hardened filter paper, and the precipitate washed by decantation with water

containing a little ammonium acetate or nitrate. The filter paper is opened out, laid on the convex side of a "clock glass," and the sulphides dissolved or rinsed from it into the beaker containing the main precipitate with as little as possible of a mixture of two parts concentrated hydrochloric acid and one part water, in which potassium chlorate has been previously dissolved. The contents of the beaker are then digested until perfect solution is attained, and the excess of chlorine expelled.

The subsequent separation of the antimony and tin is effected by one or other of the methods described in Chapter X. Of these the precipitation of the antimony from oxalic acid solution is the one most commonly used, though not perhaps the best. It gives excellent results in the antimony determination, but provides a filtrate in which the electrolytic determination of tin is practically the only available method; in the authors' hands the results were, on the whole, unsatisfactory.

The Precipitate.—The filter and precipitate are removed from the funnel and treated with hot 1.20 nitric acid until the liquid is clear. The pulp and particles of separated sulphur are filtered out, well-washed, dried and ignited, and any small residue added to the nitric acid solution. This is treated with 2 or 3 c.c. of concentrated sulphuric acid, and the liquid evaporated to fumes; the lead sulphate is then collected as usual. Copper is removed from the filtrate as sulphide, and determined iodimetrically. Iron and zinc are determined as already described under brass, &c.

For works' purposes, the separation of antimony and tin from a solution of their sulphides in hydrochloric acid and potassium chlorate is seldom attempted. Quite satisfactory results are obtained by the volumetric bromate method for antimony without a separation, and the same applies to the volumetric iodine titration for tin. The solution containing the mixed metals is therefore made up to a definite volume, and then divided into two parts, which are usually unequal in amount. The greater tin content of the majority of the alloys demands the smaller part, but the

exact proportions are a matter for individual decision, which is governed by the size of the antimoniferous residue left after the original opening-out with hydrochloric acid.

Determination of Arsenic in Alloys

Arsenic occurs as an impurity in most commercial metals, and therefore also in their alloys. The actual amount should not exceed a few hundredths per cent., since the physical properties of metals and alloys are profoundly modified by the presence of arsenic. Reliable methods for the determination of this element in raw materials are thus of great value, and fortunately there are several. These depend either on the fact that arsenic can be completely expelled in the form of trichloride from its hydrochloric acid solutions by merely boiling them, or on the preferential and quantitative precipitation of the trisulphide from cold and highly concentrated hydrochloric acid solutions. Advantage is also taken of the fact that if an acid solution containing a ferric salt and a small quantity of arsenic (As^v) is made alkaline, the ferric hydroxide which separates always contains the arsenic. In this way zinc, nickel, and copper, for the greater part, can be separated.

I. General Method.—Tin, antimony, lead and copper, and their alloys, are decomposed by a solution of ferric chloride in 25 per cent. hydrochloric acid, and the addition to the solution of potassium bromide materially hastens the removal of arsenic trichloride by the subsequent boiling. A suitable and simple apparatus is furnished by a flask provided with a stoppered funnel and a delivery tube leading to a water-jacketed glass worm.

The finely divided sample is placed in the flask together with the ferric chloride crystals and solid potassium bromide, and 200 c.c. of the acid run in from the funnel. The mixture is shaken round until the solid reagents are dissolved, connection made with the condenser, and the mixture briskly boiled down to a bulk of about 50 c.c. The distillate of 150 c.c. contains the arsenic. For each gram of drillings, 3 grams of

potassium bromide and 8 grams of ferric chloride crystals are used, the same volume of acid, consistent with complete decomposition, being used for larger amounts of the alloy. The method is a slight modification of that of Ducru.¹ The determination of the arsenic in the distillate can be made in a number of ways, of which the following are the most important.

(A) The acid solution is made alkaline by adding a strong solution of caustic soda, then just acid again by hydrochloric acid, and 20 c.c. of a saturated solution of sodium bicarbonate, free from normal carbonate or hydrate, added. The arsenic is then determined by titration with an iodine solution of N/50 strength and the usual starch indicator.

(B) A brisk current of hydrogen sulphide is passed through the cold distillate for about 15 minutes, the precipitated arsenic trisulphide filtered through asbestos, and washed first with cold dilute hydrochloric acid, and finally once or twice with cold water. The precipitate and filter are then transferred to a large beaker, 600 to 700 c.c. of distilled water added, and the liquid boiled vigorously until the volume is reduced to less than 50 c.c. The asbestos is then strained off through another small pulp filter of the same material, the filter washed well with water, and the arsenious acid in the filtrate, resulting from the hydrolysis of the sulphide (see p. 112), determined by titration with iodine after adding the usual bicarbonate solution.

(C) The arsenic is precipitated as sulphide as in (B), filtered through asbestos, and washed with dilute hydrochloric acid. The precipitate and filter are then transferred to a small beaker, about 10 c.c. of concentrated nitric acid added, and the mixture gently heated for a short time until nitrous fumes are expelled. Water is then added, and the asbestos strained off and washed. The filtrate is then evaporated to dryness, and the residue dissolved in a small volume of water. The arsenic is then determined gravimetrically by precipitation with magnesia mixture in the manner described on

¹ *Chem. Zeit.*, 37 (1903), 49.

p. 120. Alternatively, a few drops of a solution of stannous chloride are added, and the arsenic determined *via* the Bettendorff reaction, as described on p. 124.

(D) The arsenic is precipitated as trisulphide, washed, and dissolved from the filter by adding 20 c.c. of 3 per cent. hydrogen peroxide containing 5 c.c. of a 10 per cent. solution of caustic soda. The arsenic is then conveniently determined as magnesium pyroarsenate.

Method II.—Applicable to brass, bronze, and German silver. Five grams of the alloy, contained in a conical flask of about 300 c.c. capacity, are dissolved in 50 c.c. of aqua regia, 2 or 3 decigrams of ferric chloride or their equivalent in the form of bar iron added, and when all is dissolved the solution is diluted with 50 c.c. of water. The solution is heated, and whilst hot treated with a saturated aqueous solution of sodium carbonate until a small but permanent precipitate is obtained, containing the arsenic associated with the iron and some copper, &c. It is then filtered out, washed with hot water, dissolved from the filter with hot dilute nitric acid, and the solution thus obtained evaporated to dryness. The residue is dissolved in cold concentrated hydrochloric acid, a few milligrams of stannous chloride crystals added in order to reduce the arsenic acid, and the liquid saturated with hydrogen sulphide. The precipitated arsenic trisulphide is filtered through asbestos, washed several times with cold concentrated hydrochloric acid, and afterwards with water. The subsequent operations are those described under (C) of Method I.

Method III.—Applicable to white metal alloys. Two grams of the alloy are dissolved in 75 c.c. of concentrated hydrochloric acid, to which a few crystals of potassium chlorate have been previously added. A current of chlorine may be used instead of potassium chlorate, the decomposition in either case being conducted in the cold or with the application of gentle heat only. When the alloy is completely dissolved the excess of chlorine is expelled, the solution cooled, stannous chloride added, and the arsenic precipitated as before by means of hydrogen sulphide. The expulsion of the chlorine by boiling should not be unduly

prolonged, since this would result in reducing the acidity of the solution and subsequent contamination of the precipitate with antimony sulphide. In any case it is advisable, before passing hydrogen sulphide through the cooled solution, to add more concentrated hydrochloric acid. The subsequent operations are those already described. The best method of estimation in this case is the Bettendorff precipitation.

Method IV.—Applicable to special arsenical alloys containing more than 0.2 per cent. of arsenic. The preliminary operations, up to the evaporation to dryness of the nitric acid solution of the arsenic trisulphide precipitate, are the same as in preceding methods, except that a larger amount of stannous chloride (one gram) is used. One gram of an alloy containing about 1 per cent. of arsenic is a suitable amount to work upon; proportionally larger or smaller amounts are used in other cases, the amount of hydrochloric acid remaining constant. In alloys containing much tin the presence of more than half a per cent. of arsenic results in the formation of a brown scum-like precipitate on the side of the beaker during the initial stages of decomposition. This is the arsenic-tin compound of the Bettendorff reaction.

The dry residue of arsenic acid, obtained by evaporating the nitric acid solution of the arsenic trisulphide, is dissolved in water, the solution made faintly alkaline with ammonia, and then just acid again with a drop or two of dilute nitric acid. Ten c.c. of ammonium acetate and the same amount of acetic acid are added, the solution warmed and treated with an excess of a solution of silver nitrate. At first there is generally a precipitation of white silver chloride, but this is followed at once by the chocolate-coloured arsenate. The silver chloride is due to the presence of chlorine in the precipitated arsenious sulphide. It does not affect the subsequent operations which involve the dissolving of the arsenate from the filter and determination by titration with ammonium thiocyanate as described on p. 124.

Stellite

This alloy consists essentially of cobalt and chromium, and is supposed to have the composition of 75 per cent. cobalt and the rest chromium. It is generally impure, the impurities being iron, manganese, silicon, and sulphur. Originally it was put on the market as a substitute for hard steel, as it was claimed that the best cutlery could be made quite as well from this alloy as from steel, whilst the tedious process of hardening and tempering could be avoided since the stellite articles would be just cast and ground. It is certainly a very hard material, not at all easily—in fact very difficultly—machined, whilst it is not of much use to heat-treat it. Up to the present, the cutlery has not been transferred from the steel trade to the stellite, though the hardness and toughness of the alloy are properties that may be of considerable use. Generally speaking, the more chromium present in the mixture, the harder it is. Two typical analyses made by the authors are given below :

	i.	ii.
Cobalt . . .	78·42	75·08
Iron . . .	2·46	2·21
Manganese . .	2·63	4·48
Chromium . .	15·27	17·22
Sulphur . . .	0·88	0·93
Phosphorus . .	0·06	0·06
Silicon . . .	0·11	0·105

The alloy is not at all easy to dissolve. It goes quite readily in concentrated hydrochloric acid, but this is almost the only acid that will attack it. Sulphuric acid (25 per cent.) has an action upon the metal, but it is very slow—too much so to be of real use in opening out for analysis. Nitric acid has practically no action at all upon the alloy, whilst the attack of aqua regia is still slower than that of the sulphuric acid. For all analytical purposes the alloy must be attacked with hydrochloric acid first, and then this acid removed if it is necessary for the purposes of the process employed.

Determination of Cobalt, Chromium, Manganese, and Iron.—The determination of the cobalt is best performed along with those of the iron, manganese, and perhaps chromium—all from one opening-out of the alloy, though the alternative method given below for the chromium will be found in general to be more suitable. Dissolve 1 gram of the alloy in hydrochloric acid, and evaporate the solution to low bulk to remove the excess of acid. Dilute the solution, and filter off any silica, &c., allowing the liquid to fall into a graduated flask (200 c.c.). Take 50 c.c. of the solution (when made up to the mark), and transfer to a 20 oz. beaker. Carefully neutralise the solution with ammonia, leaving a faint excess of acid. Warm the solution, and add to it about 8 grams of ammonium oxalate. This will require that the volume be increased to at least 200 c.c. with hot water. When all the ammonium oxalate has dissolved, place the electrode in the beaker and electrolyse it warm, using current density of 1·5 to 1·9 and an E.M.F. of 3·3 to 3·7 volts. The electrolysis takes about three hours, and in that time about one-fifth of a gram of cobalt may be deposited easily. The deposit contains any iron that was present in the alloy besides the cobalt, whilst the chromium remains in the solution. The manganese is precipitated on the anode as the peroxide, but very frequently becomes detached and floats about the solution. Occasionally, too (but very rarely), a precipitate of aluminium hydroxide is found in the liquid. When the deposition is finished (test with sodium or ammonium sulphide), carefully remove the kathode, washing it with a fine jet, and allowing the washings to fall into the beaker in which the chromium remains. Keep the anode and this solution aside.

Dry the kathode carefully with alcohol, and weigh it. Dissolve the deposit from the platinum with a little warm nitric acid (sp. gr. 1·20). Dilute the solution, and add 3 or 4 grams of ammonium chloride, then an excess of ammonia. Warm the solution to allow the precipitated ferric hydroxide to gather in flocks, and then filter. Redissolve the precipitate in hydrochloric acid, and again add the ammonium chloride and ammonia. Collect the precipitate, wash, dry,

ignite, and weigh it as ferric oxide. Calculate this to iron, and subtract from the weight of the combined deposit of iron and cobalt. This gives the percentage of iron and of cobalt.

From the anode carefully remove all the deposit of manganese peroxide, allowing it to fall into the beaker containing the chromium solution. Filter this through a paper, and wash very thoroughly with a dilute solution of sodium carbonate. Finally, wash with hot water, ignite the precipitate gently, and weigh it. This is trimanganic tetroxide and chromic oxide. Dissolve the precipitate in nitric acid (sp. gr. 1.20), and filter the liquid (the chromic oxide is not likely to dissolve). When the filtrate is quite cold, add about 2 grams of sodium bismuthate, and shake the mixture for about two minutes. When it has quite settled, filter through asbestos pulp, and wash with 2 per cent. nitric acid by decantation. Titrate the sodium permanganate produced in the filtrate with $\frac{N}{30}$ ferrous ammonium sulphate and potassium permanganate. From the titration calculate the manganese content of the alloy (1 c.c. $\frac{N}{30}$ $\text{KMnO}_4 = 0.00036$ gram Mn).

When the manganese is calculated to Mn_3O_4 and subtracted from the weight of mixed precipitate, the weight of chromium occluded by the manganese peroxide may be calculated and added to the result obtained below.

The chromium filtrate contains the metal as ammonium chromate, and along with it a certain quantity of ammonium carbonate and some excess of ammonium oxalate. It must be acidified with sulphuric acid, and then boiled for several minutes. When the evolution of gas ceases, boil for two or three minutes more, and then cool. When quite cold, titrate with $\frac{N}{10}$ ferrous ammonium sulphate, using the potassium ferricyanide indicator. The titration must not be overshoot at all, or else the result is useless, since the presence of the ammonium oxalate renders it impossible to bring back with potassium permanganate. With the correction to be applied from above, this gives the chromium content of the alloy.

An alternative process, if the chromium is the only

element aimed at, is to use less ammonium oxalate—about 4 grams—for the electrolysis. When the cobalt, iron, and manganese have been removed, the solution is acidified and boiled. Then solid potassium permanganate is added to the production of a permanent precipitate, and the solution treated in the way described below in the direct method for chromium.

Direct Determination of Chromium.—This determination is obviously volumetric, and is perhaps the most satisfactory. Dissolve 1 gram in the minimum quantity of hydrochloric acid, oxidise with a few drops of nitric acid, and when quite dissolved add 3 or 4 c.c. of strong sulphuric acid (diluted to 20 c.c.). Boil the solution until fumes appear. When cold, dilute with hot water to 150 c.c., boil the solution, and add a strong solution of potassium permanganate until a permanent precipitate is produced or until the solution has a permanent purple colour. Boil the whole for four or five minutes, and remove from the plate. Drop into the liquid about a quarter of a gram of manganous sulphate, a few milligrams at a time. (The requisite amount of the salt is certainly reached when the precipitate appears to turn from brown to black.) Boil for another couple of minutes, then allow the precipitate to settle, and filter the solution through asbestos pulp into a 500 c.c. graduated flask. Wash thoroughly with hot water, and when cool make up to the mark. Take off two separate portions of 100 c.c. and titrate with $\frac{N}{10}$ ferrous ammonium sulphate and potassium permanganate. In order to render the solution more free from the cobalt colour near the end point, a few crystals of nickel sulphate should be added before the titration is commenced. Converting the ferrous sulphate to permanganate

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0.001736 \text{ gram chromium.}$$

Determination of Silicon.—The percentage of silicon in the alloy is not very great, but is sufficient to warrant its determination. Dissolve 4 grams of the alloy in concentrated hydrochloric acid in a 20 oz. beaker. Evaporate the solution to dryness, and bake it strongly for about twenty

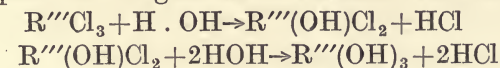
minutes after it has become dry. When cold, add to the dry baked mass about 25 c.c. of strong hydrochloric acid, and boil until the oxides and chlorides have all gone into solution. Dilute the solution with an equal bulk of hot water, and filter through a paper or through pulp. Wash the filter alternately with hot 50 per cent. hydrochloric acid and with cold water. The beaker must be cleaned very thoroughly with a policeman, or else much silica will be left behind adhering to the sides in almost invisible particles. Dry the filter, and ignite in a porcelain crucible, weighing by difference.

Determination of Sulphur.—Sulphur is estimated most satisfactorily by a volumetric process. The most suitable one is the iodine titration. Fit a large globular flask with a sound rubber stopper pierced by two holes. One of these should carry a thistle funnel and the other an outlet tube bent twice at right angles, and cut off fairly short after the second bend. Attach to this bend, by a rubber tube, a sufficient length of glass tubing to reach down to the bottom of a glass cylinder. The flask should be able to rest on the corner of the hot plate, when the tube almost touches the bottom of the cylinder. In the cylinder place 20 c.c. of a solution of cadmium chloride containing 20 grams of the salt in a litre of 50 per cent. ammonia solution. Dilute the 20 c.c. of solution to 200 c.c. with cold water. Place 1 gram of the alloy in the flask, make all the connections, and then pour into the evolution flask 50 c.c. of hot concentrated hydrochloric acid. Allow this to boil until all the alloy is dissolved. The evolved sulphuretted hydrogen is trapped in the cadmium chloride solution, as the yellow cadmium sulphide. When all the alloy is dissolved, disconnect the long tube at the rubber joint, and pour the whole of the contents of the cylinder into a large flask, carefully ensuring the removal of all the cadmium sulphide. Add hydrochloric acid in slight excess to this mixture, and at once titrate the hydrogen sulphide with standard iodine solution, using the usual starch emulsion as indicator. The iodine solution should contain two grams per litre, and of this 1 c.c. is equivalent to 0.000254 gram of sulphur.

Aluminium-Zinc Alloys

Alloys of aluminium and zinc, containing 15 to 25 per cent. of zinc along with some copper, are in use for various purposes in which lightness is of especial value. Spur gears and other machinery parts are among these cases. The analysis of the alloys, which on the surface might appear to be very easy, is not at all simple unless recourse be had to the electrolytic process outlined below. The two principal metals appear in very different groups in the schemes of qualitative analysis, but the quantitative separation of these metals is by no means so simple as the qualitative is made to appear. So far as the differences of solubility of these salts is concerned, there is very little that can be of real use. Further, the aluminium compounds are hydrolysed so easily, producing basic precipitates or even precipitates of the hydroxide if the circumstances permit, that high adsorptive power is almost universal in precipitates of this metal. Both zinc and aluminium are characterised by weak basic and very weak acid properties. This latter property is seen in the ease with which their hydroxides are dissolved by the caustic alkalis, producing solutions of zincates or aluminates, compounds in which the oxides of the metals function as acids.

The salts of the two metals have a very different degree of stability in aqueous solution, those of zinc showing a great superiority over those of aluminium, being hydrolysed very much less easily. These properties are shared by the other metals of the respective groups in which the two metals are found. Iron and chromium are very similar to aluminium, whilst cobalt, nickel, and manganese follow zinc. This fact has given rise to a general method of separation of these two groups—which is to allow the hydrolysis of the trivalent metals to take place under circumstances in which it may reach completion. In general the reaction is of the type



By the law of mass action, either or both of these reactions may be driven to completion if the hydrochloric acid is

removed from the solution and is not replaced by any other strong acid. The recognised reagent employed to do this is barium carbonate. (*N.B.*—Sulphuric acid must be absent from the solution, or disaster in the shape of barium sulphate will follow.) This salt is added as an emulsion to the solution, which is not heated, and the mixture shaken thoroughly. When the action is complete, the precipitate of excess barium carbonate and $R'''(OH)_3$ is removed from the solution, in which the divalent metal will be found. Generally speaking, the precipitate is not well suited to the estimation of the trivalent metals. This is a very accurate separation if carefully carried out, provided that there is only a small quantity of the two metals present in the original solution, but it is not a particularly neat or attractive one.

In addition to this general property of the trivalent metals—*i.e.* the tendency to hydrolysis—another common one, which is not shared by the divalent metals, manganese, nickel, cobalt, and zinc, is the insolubility of the basic acetates. This may be made the basis of a method of separation, but it bristles with difficulties. Primarily, the precipitates of the trivalent metals are invariably of the form most given to adsorption of the other basic radicles in the solution, and in consequence some of these latter are almost always found in the precipitate. Secondly, although the acetates of the divalent metals are soluble at the temperature of boiling water, their temperature of precipitation depends somewhat upon the presence or otherwise of an acetate in the solution. If any large quantity of one of these compounds is present, the temperature of precipitation is lowered very much, and may result in the presence of some quantity of these metals in the precipitate. This means that in general two precipitations are necessary if a satisfactory separation is to be made. Iron and manganese may be separated practically completely at one precipitation, but zinc is the worst of the divalent metals to separate, and perhaps aluminium is the worst of the trivalent ones. In the case of these two metals, two precipitations are essential.

A very much more attractive process is one that has been developed by Havens from the work done by Gooch

and Havens upon the precipitation of aluminium chloride. These workers found that crude aluminium chloride may be freed from every trace of a ferric salt by dissolving it in the least possible amount of water and then saturating the cooled solution with hydrochloric acid gas. This precipitates the aluminium chloride, and it may be filtered out on to asbestos and washed with the strongest hydrochloric acid available. If the salt prepared thus be dissolved in water and tested with ammonium thiocyanate, no trace of iron can be detected, but a little aluminium is found to be left in the solution, the degree of insolubility being too low for purposes of analysis. Extending this work,¹ they experimented with a mixture of equal parts of ether and of hydrochloric acid of the highest possible concentration. In this they found that the solubility of aluminium chloride amounted approximately to five parts of the hydrated salt $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (corresponding to one part of the oxide) in 125,000 parts of the mixture. The quantitative procedure as developed finally by these workers was to provide the estimation of aluminium in a mixture of aluminium and iron. A solution of the chlorides containing about 0.15 gram of the mixed metals was concentrated as far as possible. This was made up to 15 to 25 c.c. with concentrated hydrochloric acid. The solution was kept cool, and then saturated with hydrogen chloride. An equal volume of ether was then introduced, after which the solution was again saturated with hydrogen chloride. This precipitated the aluminium chloride as crystals, which were collected on asbestos, and washed with a mixture of equal parts of concentrated hydrochloric acid and ether, which had been saturated previously with hydrogen chloride. The precipitate was dried carefully at 150°C . for half an hour, then covered with a layer of 1 gram of pure mercuric oxide, and ignited. It was weighed finally as alumina. Havens² has extended the process to the separation of aluminium from zinc, with the estimation of each of the metals. After separating the aluminium exactly as above, the zinc is obtained in the filtrate by evaporation

¹ Gooch and Havens, *Amer. Journ. Sci.*, 4, ii. 416.

² Havens, *Amer Journ. Sci.*, 4, vi. 45.

to dryness several times with strong nitric acid, in a porcelain vessel. After this it is ignited to zinc oxide, and weighed as such.

All these methods mentioned above depend upon the precipitation of the aluminium, leaving the zinc in the filtrate to be estimated subsequently. Some methods have been proposed, however, which depend upon the precipitation of the zinc. One of the best known of these is the precipitation of the zinc as zinc sulphide. This compound is only insoluble in solutions containing a very small concentration of H^+ ions. It is quite insoluble in alkaline solutions, and if this solution is used for the precipitation care must be taken to avoid the precipitation of aluminium along with the zinc. In the section on the estimation of zinc (p. 166), it has been pointed out that the concentration of the H^+ ions in solutions of weakly dissociated acids accompanied by their neutral salts is also suitable for the precipitation of zinc sulphide. These latter conditions have been utilised by Hampe¹ for the separation of aluminium and zinc. More frequently, however, a solution in which the aluminium is held up as an aluminate by an excess of caustic alkali is employed. Seligmann and Willott² dissolve half a gram of the alloy in 25 c.c. of a 25 per cent. solution of caustic soda. This is diluted to 300 c.c. with boiling water, and the clear liquid decanted. If any residue is found (which will happen almost always), it is dissolved in hydrochloric acid and then re-precipitated with an excess of caustic soda. The precipitate is filtered out, and the second filtrate added to the first. Through this solution a stream of hydrogen sulphide is passed until a skin begins to form at the point where the bubbles of gas burst, thus showing that aluminium hydroxide is being precipitated along with the zinc sulphide. The precipitate is then filtered and washed with water containing ammonium chloride and sulphuretted hydrogen. It is then dissolved in 8 c.c. of hydrochloric acid, and to the solution 5 grams of ammonium chloride is added, then 250 c.c. of hot water. The zinc is then titrated with

¹ Hampe, *Chem. Zeit.*, 9 (1885), 543.

² Seligmann and Willott, *Journ. Soc. Chem. Ind.* (1905), 24, 1278.

potassium ferrocyanide (*cf.* p. 168). [It may be noted here that the direct titration of a solution containing zinc and aluminium by the potassium ferrocyanide method is not suitable for these alloys. The presence of aluminium in the quantities found in these mixtures renders the process impossible.]¹

The other method of separating these metals by the precipitation of zinc—and by far the most convenient of all the separations—is the electrolytic process. In the section upon pure zinc solutions (p. 163), details of many methods for the precipitation of the zinc have been given, and in all these cases the presence of aluminium does not interfere with the satisfactory deposition. Fischer² has tested these methods with a view to their rapidity and accuracy. He states that the sulphuric or acetic acid solutions in the presence of these neutral salts, and the solutions of the alkaline zincates, give the most satisfactory results. The solutions containing potassium cyanide give uncertain results. Sturm³ gives a preference to the deposition from alkaline hydrate solutions. He states that aluminium cannot be detected in the deposit, but that it must be assumed to be present in small quantities. As to the accuracy of the first part of the statement, the authors can vouch, the deposits being quite free from aluminium so far as the tests can show. One conspicuous advantage of this method is that the solution which remains after the removal of the zinc is quite well fitted to the determination of the aluminium (*cf.* below).

The analysis of the alloys should include the determinations of aluminium, zinc, iron, manganese, copper, and silicon.

Zinc and Aluminium.—Dissolve 1 gram of the alloy in hydrochloric acid, and boil down the solution to remove the excess of the acid. Dilute with water to about 60 c.c., and then add a strong solution of caustic soda until the precipitate which is formed is redissolved with the exception of the brown flocks of ferric hydroxide (*i.e.* add caustic soda

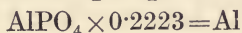
¹ *Cf.* Miller and Hall, *School of Mines Quarterly*, xvi., No. 3.

² Fischer, *Electro analytische Schnell Methoden*. Enke, Stuttgart.

³ Sturm, *Dissertation*. Aachen, 1904.

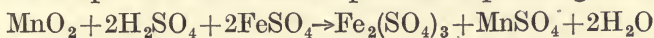
solution until the addition of a further few c.c. has no apparent effect in reducing the turbidity of the solution). Filter the solution, and wash the precipitate with hot water. Redissolve the precipitate in a little hydrochloric acid, and repeat the precipitation with the strong solution of caustic soda. Combine the two filtrates, and make up to about 300 c.c. Electrolyse the solution with current density 0.8 and E.M.F. 4.0 volts. (*N.B.*—The platinum kathode must be covered with a thin layer of copper prior to making the deposition.) The deposition should be finished in from three to four hours (test with sodium sulphide). Remove the kathode, and obtain the zinc directly by gain in weight.

Take off the filtrate, and fractionate it from 1000 c.c. to 100 c.c. Acidify the portion taken with hydrochloric acid, and add 1 or 2 c.c. in excess. Dilute to not less than 300 c.c., heat the solution to boiling, and add 2 grams of sodium phosphate. When just boiling, add gradually 10 grams of sodium thiosulphate, and then 5 c.c. of ammonium acetate. Boil the mixture for about twenty minutes. Filter the liquid through pulp, and wash with hot water containing a trace of ammonium phosphate, finishing with hot water. Ignite the precipitate gently at the mouth of the muffle. Redissolve the residue in hydrochloric acid, filter off any silica, &c., and dilute the solution to 150 c.c. Neutralise with ammonia until a turbidity appears, then just remove this with hydrochloric acid, leaving a very slight excess. Bring the liquid to the boil, and precipitate with 2 grams of sodium thiosulphate. Filter off the precipitate, and again ignite gently to aluminium phosphate, weighing as such.



Manganese and Zinc.—Dissolve 1 gram of the alloy in 30 c.c. of dilute hydrochloric acid, and add 25 c.c. of strong nitric acid. Evaporate this solution to 10 c.c., add to it 50 c.c. of nitric acid, and boil the solution. Then add gradually 5 grams of potassium chlorate until the whole of the manganese is precipitated as the black hydrated peroxide. Dilute the solution with hot water, and then filter off the precipitate of manganese on to a filter paper, washing it

with dilute nitric acid at first and finally with a little hot water. Transfer the whole of the paper and precipitate to a flask containing a known quantity of ferrous sulphate and some sulphuric acid. Shake the mixture until the precipitate has all dissolved, and then titrate the excess of ferrous sulphate with standard potassium permanganate.



This equation assumes that the precipitate is accurately of the composition MnO_2 . This is more than doubtful, and in consequence it is necessary that an empirical factor for the $\frac{\text{N}}{10}$ ferrous sulphate or the $\frac{\text{N}}{10}$ potassium permanganate be obtained by working the process on a synthetic solution of composition similar to the one provided by the alloy. If this is done, the results obtained are quite satisfactory.

Evaporate the filtrate from the above process to dryness, but do not bake it. When cold, add 7 grams of ammonium chloride, 25 c.c. of hot water, and 15 c.c. of strong ammonia. Boil the solution for a short time, being careful to break up the lumps of the crystals with a policeman. Filter the solution, and wash the precipitate several times with a boiling 1 per cent. solution of ammonium chloride. To the filtrate add 25 c.c. of strong hydrochloric acid and 40 grams of test lead. Stir the liquid until it is quite colourless, and then for a minute longer. Titrate the zinc with potassium ferrocyanide in the usual way, after diluting considerably (p. 168).

If only the manganese is required, it may be obtained from the nitric acid solution prepared above by either of two other processes. First, the manganese in the solution may be oxidised to permanganic acid by the addition of sodium bismuthate. The solution should be cold, and about 3 grams of the sodium bismuthate should be added. It is then shaken up, and, after allowing the precipitate to settle, is filtered through asbestos, washed with 2 per cent. nitric acid by decantation, and the permanganic acid in the filtrate titrated with ferrous sulphate and potassium permanganate. Another method is to estimate the manganese along with the copper. After adding the nitric acid in the first case to the hydrochloric acid solution, evaporate almost to dryness.

Add a little more nitric acid, and again evaporate almost to dryness. Add about 100 c.c. of 15 per cent. nitric acid, filter the solution, and electrolyse the filtrate with current density 1.0 to 1.5 and E.M.F. 3 to 4 volts. The copper is found on the kathode, and the manganese as peroxide on the anode. The latter deposit may be removed by a policeman, filtered, and ignited to Mn_3O_4 .

Silicon, Copper and Aluminium.—Attack 1 gram of the alloy with 30 c.c. of mixed acid, and evaporate the solution to fumes. (The mixed acid is made up of 100 c.c. nitric, 300 c.c. hydrochloric, and 200 c.c. sulphuric acid with 400 c.c. water.) Take up the cold mass in 100 c.c. of water and a little sulphuric acid. Filter out the silica, and wash with dilute hot sulphuric acid and hot water. Ignite the residue in a platinum crucible, and weigh. Add a few drops of hydrofluoric acid, evaporate away the excess, again ignite, and weigh. The difference is the silica.

$$\text{SiO}_2 \times 0.47 = \text{Si}$$

Fuse the residue from the hydrofluoric acid attack with a little sodium carbonate, and, after leaching out with water, add to the original filtrate from the silica. Electrolyse the solution with current density 1.0 to 1.5 and E.M.F. 3 to 4 volts for the copper. The aluminium may be estimated in this filtrate by two acetate separations, followed by a precipitation as phosphate or hydroxide. This process is long and tedious, and for most purposes the percentage of aluminium is found quite as accurately as by any other means if the other elements are estimated and the difference reported as aluminium.

Iron.—Dissolve 2 grams of the sample in a solution of 10 grams of caustic soda in 150 c.c. of water. Dilute the solution to 350 c.c., and allow it to stand for an hour or two in a warm place. Filter the precipitate, and wash well with hot water. Dissolve this precipitate in a little dilute acid, then either re-precipitate with ammonium chloride and ammonia and ignite to ferric oxide, or, if sufficient iron is present, reduce it with sulphurous acid, and titrate with either potassium permanganate or dichromate.

APPENDIX

APPENDIX

Sodium Sulphide Solution.—Dissolve 20 grams of sodium hydroxide in 500 c.c. of distilled water, and then allow a stream of hydrogen sulphide to pass through the solution until it is quite saturated with the gas. When this has happened, add to the solution another equal quantity of sodium hydroxide solution of the same strength, and mix the two quite thoroughly. The solution should be kept in bottles provided with close-fitting rubber stoppers. Sodium sulphide can be purchased, and a solution of any desired specific gravity made up from it.

Ammonium Acetate.—The ammonium acetate that is directed to be used in the methods described in the various sections is made most easily from the ordinary Acid Acetic B.P., and the Liq. Ammon. Fort s.g. 0.880 of the manufacturer. Into a large beaker place 1500 c.c. of the acetic acid, and then add carefully 500 c.c. of the ammonia. Some considerable evolution of heat occurs, and the mixture should be left until cold. Then either ammonia or acetic acid should be added in small quantities until litmus paper shows the solution to be as nearly neutral as possible.

Preparation of Platinum Electrodes.—It is essential that the utmost care be taken of the platinum electrodes used in electrolytic work. Before using an electrode, it should be washed quite thoroughly in strong acid, to remove any metallic deposits that may be present. The particular acid employed will depend upon the nature of the metal that has to be removed. Very frequently nitric is the best, though at times hydrochloric is preferable. Occasionally no acid can be found to give a good attack, and in this case it is most usual to make the electrode and deposit the anode in an electrolyte of sulphuric acid, and fit in wire of brass or German silver to act as kathode. Generally this will give a complete solution of the deposit in a short time. After having removed all the metallic deposits, the electrode should be washed with distilled water and then with a solution of sodium hydroxide, to take away grease as far as possible. After again washing

thoroughly in distilled water, dry the electrode by washing in absolute alcohol, and then finally by heating to redness in an open flame. Allow to cool in a desiccator, and weigh. Exactly the same care should be taken in the case of the anode, though it is not usual to weigh it. After the deposition has taken place, the electrode should be washed quite free from electrolyte with distilled water, the water removed by washing with alcohol, and then the final washing and drying performed with ether. In this case no heating should take place, as it is bound to result in harm being done either to the deposit or to the surface of the electrode in contact with the deposit. After the deposit has been weighed, it should be removed *at once*. There is no good reason that can be advanced for leaving the deposit on the electrode for any length of time after the completion of the deposition. Special precautions must be taken in the case of electrodes used for the deposition of zinc or of nickel, these being mentioned in their respective sections.

Asbestos Pulp.—The asbestos is obtained generally from the dealers in the form of stiff fibres and shreds of some thickness. The first treatment is to scrape these threads to a fairly fine state with a knife, any hard parts or pieces being discarded. The resulting fibre should be quite soft and silky in appearance and to touch. After this it should be ignited in the muffle for about an hour. Following the ignition, place the whole in a large beaker, and pour on to the shreds sufficient hot concentrated hydrochloric acid to cover the fibres. Allow them to stand in the acid for about twenty-four hours. After this let the acid drain off, and give the pulp several washings with distilled water. (This is done easily in a large funnel carrying a filter grate, the washing being done in the funnel.) When fairly free from acid, the pulp is placed in a wide-mouthed bottle with a glass stopper, and is kept covered with distilled water. It will be found preferable in most cases to keep two varieties or qualities of pulp. The very finest should be reserved for use in the Gooch crucibles, and the more coarse for ordinary work.

Iodine Monochloride Solution.—This solution, which is used for the determination of antimony, is made quite easily from potassium iodide and potassium iodate. Add 75 c.c. of distilled water to 75 c.c. concentrated hydrochloric acid, and in 50 c.c. of the mixture dissolve 10 grams of potassium iodide. In another 50 c.c. of the mixture dissolve 6.44 grams of potassium iodate.

When each salt has gone into complete solution, mix the two, make any washings out with the 50 per cent. hydrochloric acid, adding finally the rest of this solution. A precipitation of iodine will take place, and the mixed solutions should be shaken thoroughly until all the iodine has gone into solution. Then a globule of chloroform is added to the solution. If there is any free iodine present, this globule will be coloured violet, and if this colour is seen it should be removed by the careful addition of a dilute solution of potassium iodate. Similarly, if the chloroform shows perfect freedom from iodine a little of a dilute potassium iodide solution may be added. The adjustments should be made with the two solutions until the chloroform shows the presence of a small quantity of free iodine. When this is settled quite satisfactorily, transfer to a stoppered bottle. The solution will be of a strength quite suitable to the requirements of the method.

Ammonium Molybdate Solution.—This reagent is prepared by dissolving 10 grams of molybdic acid in a mixture of 17 c.c. of ammonium hydrate of specific gravity 0.880 with 25 c.c. of water, and then pouring the solution into 125 c.c. of nitric acid of specific gravity 1.2. For use, filter off the desired amount.

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LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
40	60206	60314	60423	60531	60638	60746	60853	60959	61066	61172	11	21	32	43	54	64	75	86	97
41	61278	61384	61490	61595	61700	61805	61909	62014	62118	62221	10	21	31	42	52	63	73	84	95
42	62325	62428	62531	62634	62737	62839	62941	63043	63144	63246	10	20	31	41	51	61	71	82	92
43	63347	63448	63548	63649	63749	63849	63949	64048	64147	64246	10	20	30	40	50	60	70	80	90
44	64345	64444	64542	64640	64738	64836	64933	65031	65128	65225	10	20	29	39	49	59	68	78	88
45	65321	65418	65514	65610	65706	65801	65896	65992	66087	66181	10	19	29	38	48	57	67	77	86
46	66276	66370	66464	66558	66652	66745	66839	66932	67025	67117	9	19	28	37	47	56	65	75	84
47	67210	67302	67394	67486	67578	67669	67761	67852	67943	68034	9	18	27	37	46	55	64	73	82
48	68124	68215	68305	68395	68485	68574	68664	68753	68842	68931	9	18	27	36	45	54	63	72	81
49	69020	69108	69197	69285	69373	69461	69548	69636	69723	69810	9	18	26	35	44	53	62	70	79
50	69897	69984	70070	70157	70243	70329	70415	70501	70586	70672	9	17	26	34	43	52	60	69	77
51	70757	70842	70927	71012	71096	71181	71265	71349	71433	71517	8	17	25	34	42	50	59	67	76
52	71600	71684	71767	71850	71933	72016	72099	72181	72263	72346	8	17	25	33	41	50	58	66	75
53	72428	72509	72591	72673	72754	72835	72916	72997	73078	73159	8	16	24	32	41	49	57	65	73
54	73239	73320	73400	73480	73560	73640	73719	73799	73878	73957	8	16	24	32	40	48	55	64	72
55	74036	74115	74194	74273	74351	74429	74507	74586	74663	74741	8	16	23	31	39	47	55	63	70
56	74819	74896	74974	75051	75128	75205	75282	75358	75435	75511	8	15	23	31	39	46	54	62	69
57	75587	75664	75740	75815	75891	75967	76042	76118	76193	76268	8	15	23	30	38	45	53	60	68
58	76343	76418	76492	76567	76641	76716	76790	76864	76938	77012	7	15	22	30	37	44	52	59	67
59	77085	77159	77232	77305	77379	77452	77525	77597	77670	77743	7	15	22	29	37	44	51	58	66
60	77815	77887	77960	78032	78104	78176	78247	78319	78390	78462	7	14	22	29	36	43	50	58	65
61	78533	78604	78675	78746	78817	78888	78958	79029	79099	79169	7	14	21	28	35	43	50	57	64
62	79239	79309	79379	79449	79518	79588	79657	79727	79796	79865	7	14	21	28	35	42	49	56	63
63	79934	80003	80072	80140	80209	80277	80346	80414	80482	80550	7	14	21	27	34	41	48	55	62
64	80618	80686	80754	80821	80889	80956	81023	81090	81158	81224	7	13	20	27	34	40	47	54	61
65	81291	81358	81425	81491	81558	81624	81690	81757	81823	81889	7	13	20	27	33	40	46	53	60
66	81954	82020	82086	82151	82217	82282	82347	82413	82478	82543	7	13	20	26	33	39	46	52	59
67	82607	82672	82737	82802	82866	82930	82995	83059	83123	83187	6	13	19	26	32	39	45	51	58
68	83251	83315	83378	83442	83506	83569	83632	83696	83759	83822	6	13	19	25	32	38	44	51	57
69	83885	83948	84011	84073	84136	84198	84261	84323	84386	84448	6	12	19	25	31	38	44	50	56
70	84510	84572	84634	84696	84757	84819	84880	84942	85003	85065	6	12	18	25	31	37	43	49	56
71	85126	85187	85248	85309	85370	85431	85491	85552	85612	85673	6	12	18	24	30	36	42	48	55
72	85733	85794	85854	85914	85974	86034	86094	86153	86213	86273	6	12	18	24	30	36	42	48	54
73	86332	86392	86451	86510	86570	86629	86688	86747	86806	86864	6	12	18	24	30	36	41	47	53
74	86923	86982	87040	87099	87157	87216	87274	87332	87390	87448	6	12	18	23	29	35	41	47	52
75	87506	87564	87622	87679	87737	87795	87852	87910	87967	88024	6	12	17	23	29	35	40	46	52
76	88081	88138	88195	88252	88309	88366	88423	88480	88536	88593	6	11	17	23	28	34	40	46	51
77	88649	88705	88762	88818	88874	88930	88986	89042	89098	89154	6	11	17	22	28	34	39	45	50
78	89209	89265	89321	89376	89432	89487	89542	89597	89653	89708	6	11	17	22	28	33	39	44	50
79	89763	89818	89873	89927	89982	90037	90091	90146	90200	90255	5	11	16	22	27	33	38	44	49
80	90309	90363	90417	90472	90526	90580	90634	90687	90741	90795	5	11	16	22	27	32	38	43	49
81	90849	90902	90956	91009	91062	91116	91169	91222	91275	91328	5	11	16	21	27	32	37	43	48
82	91381	91434	91487	91540	91593	91645	91698	91751	91803	91855	5	11	16	21	26	32	37	42	47
83	91908	91960	92012	92065	92117	92169	92221	92273	92324	92376	5	10	16	21	26	31	36	42	47
84	92428	92480	92531	92583	92634	92686	92737	92788	92840	92891	5	10	15	21	26	31	36	41	46
85	92942	92993	93044	93095	93146	93197	93247	93298	93349	93399	5	10	15	20	25	30	36	41	46
86	93450	93500	93551	93601	93651	93702	93752	93802	93852	93902	5	10	15	20	25	30	35	40	45
87	93952	94002	94052	94101	94151	94201	94250	94300	94349	94399	5	10	15	20	25	30	35	40	45
88	94448	94498	94547	94596	94645	94694	94743	94792	94841	94890	5	10	15	20	25	29	34	39	44
89	94939	94988	95036	95085	95134	95182	95231	95279	95328	95376	5	10	15	19	24	29	34	39	44
90	95424	95472	95521	95569	95617	95665	95713	95761	95809	95856	5	10	14	19	24	29	34	38	43
91	95904	95952	95999	96047	96095	96142	96190	96237	96284	96332	5	10	14	19	24	29	33	38	43
92	96379	96426	96473	96520	96567	96614	96661	96708	96755	96802	5	9	14	19	24	28	33	38	42
93	96848	96895	96942	96988	97035	97081	97128	97174	97220	97267	5	9	14	19	23	28	33	37	42
94	97313	97359	97405	97451	97497	97543	97589	97635	97681	97727	5	9	14	18	23	28	32	37	41
95	97772	97818	97864	97909	97955	98000	98046	98091	98137	98182	5	9	14	18	23	27	32	36	41
96	98227	98272	98318	98363	98408	98453	98499	98543	98588	98632	5	9	14	18	23	27	32	36	41
97	98677	98722	98767	98811	98856	98900	98945	98989	99034	99078	4	9	13	18	22	27	31	36	40
98	99123	99167	99211	99255	99300	99344	99388	99432	99476	99520	4	9	13	18	22	26	31	35	40
99	99564	99607	99651	99695	99739	99782	99826	99870	99913	99957	4	9	13	17	22	26	31	35	39
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

ANTI-LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·00	10000	10023	10046	10069	10093	10116	10139	10162	10186	10209	2	5	7	9	12	14	16	19	21
·01	10233	10257	10280	10304	10328	10352	10375	10399	10423	10447	2	5	7	9	12	14	17	19	21
·02	10471	10495	10520	10544	10568	10593	10617	10641	10666	10691	2	5	7	10	12	15	17	20	22
·03	10715	10740	10765	10789	10814	10839	10864	10889	10914	10940	3	5	8	10	13	15	18	20	23
·04	10965	10990	11015	11041	11066	11092	11117	11143	11169	11194	3	5	8	10	13	15	18	20	23
·05	11220	11246	11272	11298	11324	11350	11376	11402	11429	11455	3	5	8	11	13	16	18	21	24
·06	11482	11508	11535	11561	11588	11615	11641	11668	11695	11722	3	5	8	11	14	16	19	21	24
·07	11749	11776	11803	11830	11858	11885	11912	11940	11967	11995	3	5	8	11	14	16	19	22	25
·08	12023	12050	12078	12106	12134	12162	12190	12218	12246	12274	3	6	8	11	14	17	20	22	25
·09	12303	12331	12360	12388	12417	12445	12474	12503	12531	12560	3	6	9	11	14	17	20	23	26
·10	12589	12618	12647	12677	12706	12736	12764	12794	12823	12853	3	6	9	12	15	18	21	24	26
·11	12883	12912	12942	12972	13002	13032	13062	13092	13122	13152	3	6	9	12	15	18	21	24	27
·12	13183	13213	13243	13274	13305	13335	13366	13397	13428	13459	3	6	9	12	15	18	21	25	28
·13	13490	13521	13552	13583	13614	13646	13677	13709	13741	13772	3	6	9	13	16	19	22	25	28
·14	13804	13836	13868	13900	13932	13964	13996	14028	14060	14093	3	6	10	13	16	19	22	26	29
·15	14125	14158	14191	14223	14256	14289	14322	14355	14388	14421	3	7	10	13	16	20	23	26	30
·16	14454	14488	14521	14555	14588	14622	14655	14689	14723	14757	3	7	10	13	17	20	24	27	30
·17	14791	14825	14859	14894	14928	14962	14997	15031	15066	15101	3	7	10	14	17	21	24	28	31
·18	15136	15171	15205	15241	15276	15311	15346	15382	15417	15453	4	7	11	14	18	21	25	28	32
·19	15488	15524	15560	15596	15631	15668	15704	15740	15776	15812	4	7	11	14	18	22	25	29	32
·20	15849	15885	15922	15959	15996	16032	16069	16106	16144	16181	4	7	11	15	19	22	26	30	33
·21	16218	16255	16293	16331	16368	16406	16444	16482	16520	16558	4	8	11	15	18	22	26	30	34
·22	16596	16634	16672	16711	16749	16788	16827	16866	16904	16943	4	8	12	15	19	23	27	31	35
·23	16982	17022	17061	17100	17140	17179	17219	17258	17298	17338	4	8	12	16	20	24	28	32	36
·24	17378	17418	17458	17498	17539	17579	17620	17660	17701	17742	4	8	12	16	20	24	28	32	36
·25	17783	17824	17865	17906	17947	17989	18030	18072	18113	18155	4	8	12	17	21	25	29	33	37
·26	18197	18239	18281	18323	18365	18408	18450	18493	18536	18578	4	8	13	17	21	25	30	34	38
·27	18621	18664	18707	18750	18793	18836	18880	18923	18967	19011	4	9	13	17	22	26	30	35	39
·28	19055	19099	19143	19187	19231	19275	19320	19364	19409	19454	4	9	13	18	22	27	31	35	40
·29	19498	19544	19588	19634	19679	19724	19770	19815	19861	19907	5	9	14	18	23	27	32	36	41
·30	19953	19999	20045	20091	20137	20184	20230	20277	20324	20370	5	9	14	19	23	28	33	37	42
·31	20417	20464	20512	20559	20606	20654	20702	20749	20797	20845	5	10	14	19	24	29	33	38	43
·32	20893	20941	20989	21038	21086	21136	21184	21232	21281	21330	5	10	15	20	24	29	34	39	44
·33	21380	21429	21478	21528	21577	21627	21677	21727	21777	21827	5	10	15	20	25	30	35	40	45
·34	21878	21928	21979	22029	22080	22131	22182	22233	22284	22336	5	10	15	20	25	31	36	41	46
·35	22387	22439	22491	22542	22594	22646	22699	22751	22803	22856	5	10	16	21	26	31	36	42	47
·36	22909	22961	23014	23067	23121	23174	23227	23281	23335	23388	5	11	16	21	27	32	37	43	48
·37	23442	23496	23550	23605	23659	23714	23768	23823	23878	23933	5	11	16	22	27	33	38	44	49
·38	23988	24044	24099	24155	24210	24266	24322	24378	24434	24491	6	11	17	22	28	34	39	45	50
·39	24547	24604	24660	24717	24774	24831	24889	24946	25003	25061	6	11	17	23	29	34	40	46	51
·40	25119	25177	25235	25293	25351	25410	25468	25527	25586	25645	6	12	18	23	29	35	41	47	53
·41	25704	25763	25823	25882	25942	26002	26062	26122	26182	26242	6	12	18	24	30	36	42	48	54
·42	26303	26363	26424	26485	26546	26607	26669	26730	26792	26853	6	12	18	24	31	37	43	49	55
·43	26915	26977	27040	27102	27164	27227	27290	27353	27416	27479	6	13	19	25	31	38	44	50	56
·44	27542	27606	27669	27733	27797	27861	27925	27990	28054	28119	6	13	19	26	32	39	45	51	58
·45	28184	28249	28314	28379	28445	28510	28576	28642	28708	28774	7	13	20	26	33	39	46	52	59
·46	28840	28907	28973	29040	29107	29174	29242	29309	29376	29444	7	13	20	27	34	40	47	54	60
·47	29512	29580	29648	29717	29785	29853	29923	29992	30061	30130	7	14	21	28	34	41	48	55	62
·48	30200	30269	30339	30409	30479	30549	30620	30690	30761	30832	7	14	21	28	35	42	49	56	63
·49	30903	30974	31046	31117	31189	31261	31333	31405	31477	31550	7	14	22	29	36	43	50	58	65
·50	31623	31696	31769	31842	31915	31989	32063	32137	32211	32285	7	15	22	29	37	44	52	59	66
·51	32359	32434	32509	32584	32659	32734	32809	32885	32961	33037	8	15	23	30	38	45	53	60	68
·52	33113	33189	33266	33343	33420	33497	33574	33651	33729	33806	8	15	23	31	38	46	54	62	69
·53	33884	33963	34041	34119	34198	34277	34356	34435	34514	34594	8	16	24	32	39	47	55	63	71
·54	34674	34754	34834	34914	34995	35075	35156	35237	35318	35400	8	16	24	32	40	48	56	65	73
·55	35481	35563	35645	35727	35810	35892	35975	36058	36141	36224	8	17	25	33	41	50	58	66	74
·56	36308	36391	36475	36559	36644	36728	36813	36898	36983	37068	8	17	25	34	42	51	59	68	76
·57	37154	37239	37325	37411	37497	37584	37670	37757	37844	37931	9	17	26	35	43	52	61	69	78
·58	38019	38107	38195	38282	38371	38459	38548	38637	38726	38815	9	18	27	35	44	53	62	71	80
·59	38905	38994	39084	39174	39264	39355	39446	39537	39628	39719	9	18	27	36	45	54	63	72	82
·60	39811	39902	39994	40087	40179	40272	40365	40458	40551	40644	9	19	28	37	46	56	65	74	83
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

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INTERNATIONAL ATOMIC WEIGHTS, 1915

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminium . . .	Al	27.1	Molybdenum . . .	Mo	96.0
Antimony . . .	Sb	120.2	Neodymium . . .	Nd	144.3
Argon . . .	A	39.88	Neon . . .	Ne	20.2
Arsenic . . .	As	74.96	Nickel . . .	Ni	58.68
Barium . . .	Ba	137.37	Niton (radium emanation) . . .	Nt	222.4
Bismuth . . .	Bi	208.0	Nitrogen . . .	N	14.01
Boron . . .	B	11.0	Osmium . . .	Os	190.9
Bromine . . .	Br	79.92	Oxygen . . .	O	16.0
Cadmium . . .	Cd	112.40	Palladium . . .	Pd	106.7
Caesium . . .	Cs	132.81	Phosphorus . . .	P	31.04
Calcium . . .	Ca	40.07	Platinum . . .	Pt	195.2
Carbon . . .	C	12.0	Potassium . . .	K	39.1
Cerium . . .	Ce	140.25	Praseodymium . . .	Pr	140.6
Chlorine . . .	Cl	35.46	Radium . . .	Ra	226.4
Chromium . . .	Cr	52.0	Rhodium . . .	Rh	102.9
Cobalt . . .	Co	58.97	Rubidium . . .	Rb	85.45
Columbium . . .	Cb	93.5	Ruthenium . . .	Ru	101.7
Copper . . .	Cu	63.57	Samarium . . .	Sa	150.4
Dysprosium . . .	Dy	162.5	Scandium . . .	Sc	44.1
Erbium . . .	Er	167.7	Selenium . . .	Se	79.2
Europium . . .	Eu	152.0	Silicon . . .	Si	28.3
Fluorine . . .	F	19.0	Silver . . .	Ag	107.88
Gadolinium . . .	Gd	157.3	Sodium . . .	Na	23.0
Gallium . . .	Ga	69.9	Strontium . . .	Sr	87.63
Germanium . . .	Ge	72.5	Sulphur . . .	S	32.07
Glucinum . . .	Gl	9.1	Tantalum . . .	Ta	181.5
Gold . . .	Au	197.2	Terbium . . .	Tb	159.2
Helium . . .	He	3.99	Thallium . . .	Tl	204.0
Holmium . . .	Ho	163.5	Thorium . . .	Th	232.4
Hydrogen . . .	H	1.008	Thulium . . .	Tm	168.5
Indium . . .	In	114.8	Tin . . .	Sn	119.0
Iodine . . .	I	126.92	Titanium . . .	Ti	48.1
Iridium . . .	Ir	193.1	Tungsten . . .	W	184.0
Iron . . .	Fe	55.84	Uranium . . .	U	238.5
Krypton . . .	Kr	82.92	Vanadium . . .	V	51.0
Lanthanum . . .	La	139.0	Xenon . . .	Xe	130.2
Lead . . .	Pb	207.10	Ytterbium . . .	Yb	172.0
Lithium . . .	Li	6.94	Yttrium . . .	Yt	89.0
Lutecium . . .	Lu	174.0	Zinc . . .	Zn	65.37
Magnesium . . .	Mg	24.32	Zirconium . . .	Zr	90.6
Manganese . . .	Mn	54.93			
Mercury . . .	Hg	200.6			

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